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DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

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FROM HORSE-SHOE NAILS TO HIGH POWER LASERS

The Changing Role of Materials Research Laboratories

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From Horse-shoe Nails to High Power Lasers

The Changing Role of the Materials Research Laboratories

John Gleeson (A)

MATERIALS RESEARCH LABORATORIES, Maribyrnong, Victoria, as part of the Defence Science and Technology Organisation, Department of Defence are in 1977, like the Royal Australian Chemical Institute, celebrating a special Jubilee. To mark the occasion *Chemistry in Australia* presents a history of the Laboratories from its foundation to the present.

"For want of a nail the shoe was lost,

For want of a shoe ....

....

For want of a battle the kingdom was lost,

And all for the want of a horse-shoe nail."

Benjamin Franklin

Whether or not horse-shoe nails could win battles and save kingdoms would not have concerned scientists of Munitions Supply Laboratories back in 1923; they did know that nails or any other defence stores had to do the job they were designed to do, and they knew the way to ensure this was to see they met rigid standards. If they failed in test they could fail in service, so they were redesigned until they passed. Today, more than half a century later, we have watched battles won and lost, we have seen kingdoms disappear and empires crumble; instead of horses we have faster-than-sound aircraft; instead of metal nails we have super alloys and fibre-plastics composites; but across the gulf of years and technology the Laboratories' concern about quality and performance remains unchanged.

The origins of MRL go back well beyond the twenties. In 1909 Mr C. Napier Hake, then Chief Inspector of Explosives for Victoria, recommended that the Defence Department should take over surveillance of cordite and other explosives. This was a job with an inbuilt hazard for it was well known that magazines of cordite were likely to explode, especially in hot climates like that of India. He nominated one Marcus Bell as Chemical Adviser to the Department.

No one seems to have demurred at this, and in 1910 Marcus Bell moved into the Chemical Adviser's Laboratory, a former guardroom inside the south gate of Victoria Barracks, Melbourne. Today a pedestrian may view the old building, externally unchanged since the first decade of the century, through the south gate of the Barracks.

Self reliance in defence was a subject well to the fore in those early years after Federation. Deciding that Australia should produce its own cartridge fillings, the Government appointed A. E. Leighton* as

*A. E. Leighton is commemorated by the Institute by the Leighton Memorial Award in recognition of a distinguished career as a chemist, technologist and administrator.

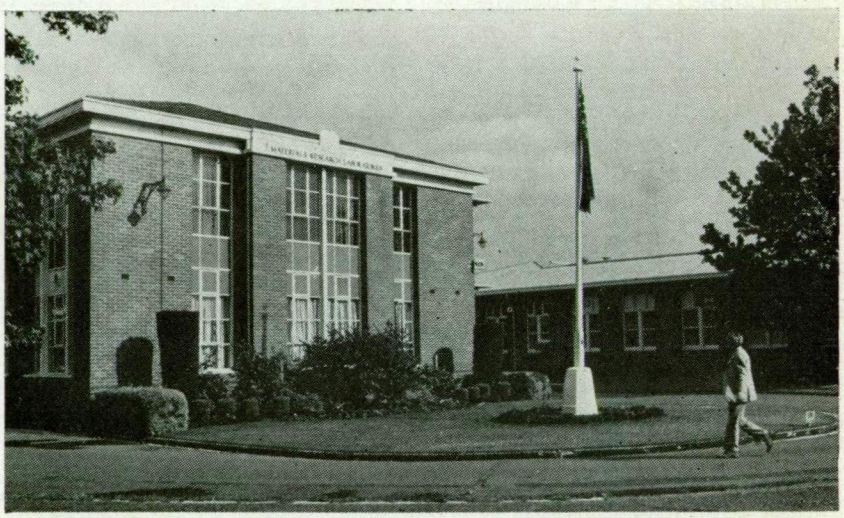


Figure 1—Materials Research Laboratories, Maribyrnong, Victoria, 1977—main entrance.

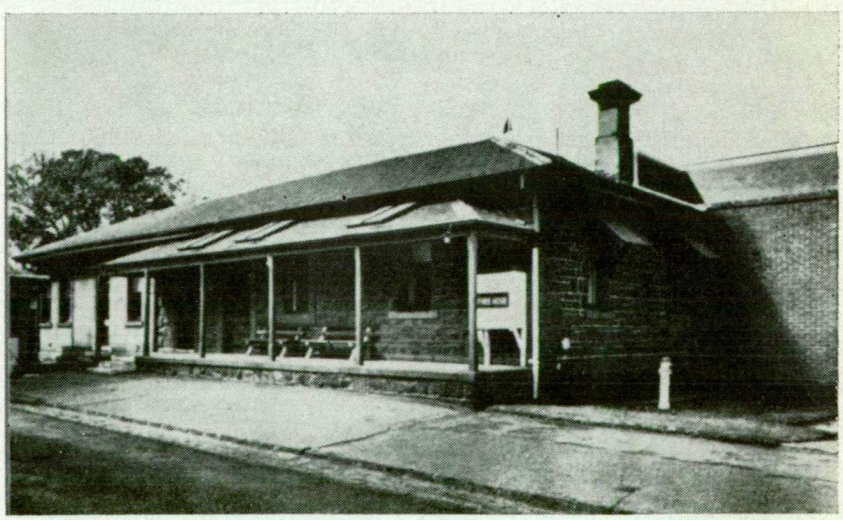


Figure 2—The Chemical Adviser's Laboratory, Victoria Barracks, St Kilda Road, Melbourne—the foundation laboratory of MRL.

manager of a new cordite factory to be built within a loop of the river using a conveniently level site of the Maribyrnong racecourse. Leighton, an able explosives man, had been assistant manager of the Cordite Factory in India where frequent skirmishes with tribesmen who were not particularly keen to join the British Empire had kept the quality of cordite high; indeed the Aruvankadu factory ranked as one of Britain's best. Leighton, who had learned his craft at Waltham Abbey, Essex where the watchword was safety, (and perhaps conditioned by the periodic magazine explosions in India), knew well that quality control was the key to safe and efficient explosives production; thus his was another strong influence in setting up the Chemical Adviser's Laboratory.

The laboratory staff in 1910 comprised Bell (Superintendent), J. T. McCormick, G. A. Ampt and R. J. Craig. In 1911, R. E. Summers, to whom we are indebted for much of this early history, replaced Craig. Summers remembers Bell as a capable planner and versatile scientist, a pleasant, cultured gentleman who in his spare time played in a string quartet. He remembers, too, his own appointment; hearing of a vacancy for a junior chemist at Bell's laboratory, he jumped on the St Kilda Rd tram and confronted Bell, who was just leaving on his honeymoon. Despite his more important engagement Bell interviewed him on the spot, accepted him and gave him his honeymoon address so that Summers could mail an official application. Bell's must be the ultimate example of combining business with pleasure.

Imperial standards

Metrology work by 1936 had grown steadily, justifying a new section severed from Physics. Quite early in its history the Metrology sub-section had acquired imperial standards of mass and length; these were the basis for a growing service to Government and Industry of checking and calibrating measuring instruments, tools and gauges, and later a calibration service for instruments used to control manufacture of munitions. Pyrometers are an important example. More important was the future need of interchangeable arms and ammunition; if Australia was to produce these for use by Britain, Commonwealth countries and perhaps USA, a high degree of precision based on master standards was essential. At its peak in the forties, Metrology Section checked 100,000 gauges annually.

Figure 3—Taken from a staff photograph of 1924. l to r: R. E. Summers, J. T. McCormick, M. Bell, A. E. Dawkins.

STORM WARNING

1938–Munich–and a warning the world could not ignore. But at least the 'peace' of Munich was a breathing space, a time to build and strengthen the levee banks before the storm exploded in September 1939. In that twelve months MSL almost trebled its staff. Then, as munitions production grew rapidly, the laboratories were forced to dilute to the limit the thin ranks of professionals with untrained and semi-trained assistants. To augment the supply of trained metallurgists, Melbourne University agreed that students in metallurgical engineering who had completed three years' study could work at MSL for the fourth year to gain a degree. An agreement with the New Zealand Government also helped to ease the shortage; as a result a number of chemists of high calibre crossed the Tasman to work at MSL.

But the solving of one problem created another—shortage of space. The building programme, though it included a large new building for Physics in 1941, and another tailored to the special needs of Chemical Defence in 1942 could not cope with staff growth, which swelled from 80 in 1938 to 1150 in 1944. MSL took over rooms in the State Laboratories and Henty House mainly for metrology work, while a new factory in Brunswick, originally built for Hilton Hosiery, became the laboratory for radiography, pyrometry, X-ray diffraction, photography and for the testing of paints, textiles, lubricants and fuels. Always there was pressure to speed the product from machine to serviceman. To achieve this, examination was decentralized by establishing Branches and Approved Test Houses both in Victoria and other States. Thus other government laboratories, universities, technical colleges and private industrial laboratories shared the workload and cut delays. Of the interstate Branches only Alexandria, NSW, remains as part of the present MRL–that at Finsbury, SA transferred to CSIRO on 1 September 1977.

Wartime demands

Pressure of war work made extra demands on MSL's scientists and engineers, who had to learn new skills and to extend their developmental work in areas of research and investigation. Exotic chemicals, unavailable in Australia, had to be synthesized. Instruments and plant, always in short supply, had to be used carefully and husbanded, for often replacement was impossible. To meet this need, workshops grew more sophisticated; as well, a new, fine workshop attracted and trained craftsmen skilled in optics and the building and repair of fine instruments.

John Gleeson (A) *graduated from the University of Melbourne (B.Sc., 1948) and joined the Laboratories in 1949. For some years he worked on protective clothing and the production of active carbon from such local sources as brown coal. More recently his duties have included forensic science, science writing and public relations.*

Apart from the vast programme of testing, MSL's wartime endeavour achieved many unique successes. Rot-proofing of canvas improved four-fold the life of tents in the tropics. At Lidcombe, where aircraft castings were tested for flaws, MSL pioneered the use of radiography in Australia. Radiography solved many problems when staff examined enemy guns, bombs and ammunition—and on one occasion a torpedo warhead from a miniature submarine that had sneaked into Sydney Harbour—by detecting faults or booby traps, thus making the task less hazardous. The explosives staff set a fine safety record; despite the number and variety of enemy weapons examined, not a single accident occurred.

From Barracks to campus

Gus Ampt deserves a mention. Well known to generations of chemistry students at Melbourne University, he was another pioneer in the Victoria Barracks Laboratory and one whose meticulous analyses marked him as a dependable authority. But late in the war Gus decided to seek his career elsewhere. At Melbourne University he found a successful one.

The Laboratory flourished, and as its reputation grew it attracted many requests for consultation and service. Bell offered its resources to other Government Departments and to industry, where help was needed in manufacturing materials directly or indirectly related to Australia's defence.

Laying foundations in UK

With World War I came the chance to gain first-hand experience in established defence laboratories overseas. First R. E. Summers went to Ministry of Munitions in England to assist in starting up and running nitro cellulose factories. Then in 1916, Bell and members of the newly formed Australian Arsenal Branch went abroad to work in and inspect factories and laboratories in Britain, India and USA. In mid-1918 a Research Laboratories group, formed in England, began plans for the Central Research Laboratories to serve the Australian Arsenal, a concept similar to Research Department, Woolwich Arsenal. The plans materialized early in 1922 when the Barracks laboratory took over the Research Buildings, Arsenal Branch, sited south of the Cordite Factory on the Maribyrnong river. The name did not last, for was not World War I the war to end all wars? Arsenals had no place in the new millenium. So the Research Buildings became the Laboratories of Munitions Supply Board, later shortened to Munitions Supply Laboratories.

Among the early recruits was A. E. Dawkins, a future Chief Superintendent, who was then holder of an 1851 Research Scholarship. During 1921-2 he visited England, choosing as his scholarship research a study of the phase rule applied to explosive filling. An apt subject, for in our explosives research today with improved TNT fillings, study of phase diagrams is still important in assessing the most effectice filling.

The new laboratories, divided into five Sections, offered technical advice and service on explosives and ammunition, Timber, General chemistry, Metallurgy, and Physics. But despite the end of the war-to-end-wars, some people remained unconvinced. With the memory still vivid of attacks by those insidious chemical weapons, chlorine, mustard gas and phosgene that burnt skin and lungs without warning, the authorities included a Chemical Defence Section under P. R. Weldon. In 1928, Weldon returned from England where he had spent some time at the Chemical Defence Establishment at Porton, Wiltshire studying war gases and counter measures. His Section began evaluating various rubber mixes for gas mask face-pieces in the Australian climate. They also evaluated various grades of bleaching powder, then the most effective material for decontaminating weapons and equipment affected by mustard gas. To push these researches further, special laboratories were built with advanced fume cupboards, filtered exhaust systems and gas sealing devices, so that toxic materials could be handled safely.

A NEW LEADER

In 1934, Bell's poor health forced him to take sick leave. The end of an era then, for the sound planner and cultured gentleman returned no more to the laboratories or to the string quartet. After Bell's death, his deputy J. T. McCormick, M.Sc., became Superintendent with A. E. Dawkins as Assistant Superintendent. McCormick is remembered as an august figure, renowned for his informal inspections. At any time he might leave his desk and stroll through the laboratories to see for himself if production and testing were running smoothly. August, but not aloof; indeed a very humane man. Despite the great increase in staff with wartime recruiting, he knew them all by name, and more than that, knew them if he met them off the area. The wartime achievement of MSL stands as his memorial.

Anti-gas respirators

An outstanding effort was that of the Chemical Defence Section whose staff of 500, cooperating with industry, produced more than a million anti-gas respirators for the armed services. The exercise was far from smooth; hitches occurred in manufacturing almost every component. There were eyepieces that cracked or discoloured; valves that failed to seal or that sealed so tightly that they exhausted the wearer, and there was the alarming occasion when the feather supply failed. The filter that removed dust particles consisted of Chinese duck down impregnated with lamp black. One day, staff inspecting supplies of feathers were startled to find that much of the stock had been ravaged by the case-making clothes moth; then came the alarming thought "What of the respirators already in service?" But luckily the lamp black had made the filters safe against insect attack. Shortly afterwards, filters of treated merino wool replaced the down filters.

For all the effort, troubles and worries the respirators were not needed, for no gas was used in the second world war. But it might have been. When the Allies took over Germany, they were shocked to find tank car loads of new chemical weapons–nerve gases–whose existence they did not suspect. German factories were geared to produce quantities of the deadly chemical which was many times more lethal than the worst of the known war gases. Had these been used the Chemical Defence project might have been most valuable. All was not lost though; from the experience with wartime respirators came the skills with industrial respirators, an area where these Laboratories have become an ultimate authority. Again a superb safety record; throughout the entire programme of testing respirators against lethal gases, there was not one incident of even minor gassing.

SWORDS TO PLOUGHSHARES

After the war came a winding down and a new role for MSL. The war years had seen secondary industry thrust ahead but now it needed scientific guidance in changing from munitions to peace-time production. After discussions between MSL and CSIRO to define the fields where each would work, the Minister authorized MSL to assist secondary industry. This decision, strongly endorsed by Prime Minister Chifley, was the keystone to the future of the Laboratories; without it MSL could have dwindled to a small unit with a watching brief on defence.

One of the first tasks came from the Universities. With record university enrolments as servicemen resumed interrupted studies, the supply of student microscopes fell far short of the demand. Drawing on its experience with optical munitions, MSL helped to prepare the specification for an Australian microscope, then designed and manufactured objectives eyepieces and substage condensers. The microscopes performed well, comparing favourably with imported instruments.

When J. T. McCormick retired in 1947, A. E. Dawkins who had joined the Chemical Adviser's staff during World War I was promoted to General Superintendent. To him fell much of the task of smoothing the change from war to peace and of preparing the ground for the special research work of the fifties and the sixties.

DRL becomes DSL

In 1948, MSL changed its name to Defence Research Laboratories, and a few years later to Defence Standards Laboratories when it became part of the new Research and Development Branch in Department of Supply. Gradually the emphasis moved from aid to industry towards a deep involvement in defence research. Not completely though, for the defence potential of industry was well known; where special resources or expertise were needed, the Laboratories were ready to help. This was evident during the Korean War.

This touches on an intermediate area where our contribution is not always recognized; where techniques conceived originally for work within the Defence charter have a spin-off bonus for primary or secondary industry, or elsewhere in the Australian scene. For instance the mass fire experiment, codenamed EUROKA. On a 20 hectare site in Queensland, more than 5,000 tonnes of waste scrub were burnt to determine, from a complex web of instruments, such data as rate of fire spread, radiant heat and evidence of fire storms. In the centre of the site, within a trench and bunker system, instruments measuring changing temperatures and toxic gas levels, shed new light on human survival in large fires. Thus EUROKA marked another step towards taming the menace of summer fires in our farmlands, forests and national parks.

A modern materials lab.

After serving 18 months as Deputy Dr F. A. Fox became Chief Superintendent in September 1957. During his term of 13 years he accelerated the change from a testing and calibrating laboratory with a limited research budget to a modern materials laboratory, well furnished with best and newest research tools. New buildings were constructed, older ones remodelled and well qualified staff recruited to pursue basic and applied research in fields appropriate to our charter. The Vietnam War accelerated these changes.

Challenging the tropics

During World War II and Vietnam, much equipment designed for service in Europe failed utterly when used in the tropics. For many years now the Defence Forces have called on our resources and skills to combat those two relentless environments, the tropics and the oceans. Both have tested our scientists in many disciplines; the list of challenging problems includes deterioration of equipment by sunlight, humidity and fungi; the study of venomous sea creatures such as the sea wasp, the ringed octopus and the stone fish; improving marine paints to keep ships free from barnacles; protective anodes to prevent corrosion; and, as a special project, restoration of historic relics of Cook's voyage that had lain deep in the Barrier Reef waters for two centuries. Success has not been swift or easy—often the solution to one problem will pose another. Thus treating a fabric to prevent rotting by fungi may cause it to disintegrate in sunlight; or a copper oxide paint effective against barnacles may form a galvanic cell in sea water and corrode the hull of a naval ship.

To support many of these research and investigational programmes the Joint Tropical Research Unit was formed in 1962 with main laboratories at Innisfail, North Queensland. The Unit was a joint undertaking between Explosives Research and Development Establishment, Waltham Abbey, Essex, England and Defence Standards Laboratories. In 1976, the Unit was transferred to Service Laboratories and Trials Division of Department of Defence. The challenge of sea and climate goes on, but year by year the laboratories can claim to have won further ground.

SOME NOTEWORTHY TASKS

Even with the change to work on special defence projects, many other projects emerged, important enough to make a strong international impact. One from the late fifties was xerography, the process of recording an image electrostatically, in a sense the physical counterpart of chemical photography. A major advance in xerography was the invention at our South Australian Branch of liquid development which had many advantages over dry powder development, then the standard method. The liquid method greatly improved resolving power and tonal gradation; with it, non-erasable images could be made without fixing as well as images in any colour or combination of colours. The many patents on our processes aroused much interest overseas; one example was when three officers from a Tokyo optical company visited the SA Branch for study and training under an agreement with the Japanese Government which licensed this company to use the processes.

On the morning of 10 July 1962, a low loader and trailer, a total weight of 45 tonnes, was crossing the new King's Bridge from South Melbourne to the City. Suddenly a span collapsed; the roadway sagged, and the $8,000,000 bridge was out of action only 15 months after its opening. Called in on the Committee of Investigation seeking the cause of the failure, DSL metallurgists studied the wrecked girders in great detail showing how the fractures had originated in the fillet welds as toe cracks which had remained undetected during original inspection and later had extended step by step during the life of the girder. Of I. J. Ferris, DSL leader in this research, the Royal Commission said "He at least was one man who really knew what he

was talking about," and acknowledged his "valuable evidence".

Restoring Cook's cannon

Another investigation outside the normal charter of DSL but one which drew on the experience of our corrosion scientists was the restoration of the Endeavour cannon. Just over 200 years ago when Captain James Cook was warily feeling his way through the Barrier Reef waters, the Endeavour struck an outcrop of rock and was pinned fast on the coral shelf. To lighten the ship in the hope of lifting her free on the next flood tide, Cook ordered that the six deck cannon be heaved overboard. For two centuries they lay there gradually becoming entombed in a vault of coral.

Just before the Cook bi-centenary, a United States team located the cannon, blasted them free and raised them. Department of Shipping and Transport asked DSL to attempt to restore the historic relics. The cannon, still coral-encrusted, were first radiographed so that important fragments would not be lost or damaged when the coral was removed. Then electrolysis in dilute sodium hydroxide solution with the cannon as cathode and mild steel as anode, removed chloride ions from the surface layers. Careful control of the current density avoided blistering of the cannon surface. Measuring chloride ion concentration in the electrolyte showed when all chloride had been removed, after which the cannon were washed exhaustively in distilled water, dried and sealed.

Dr C. Pearson, in charge of the restoration project, received an MBE award for his work.

INTO THE SEVENTIES

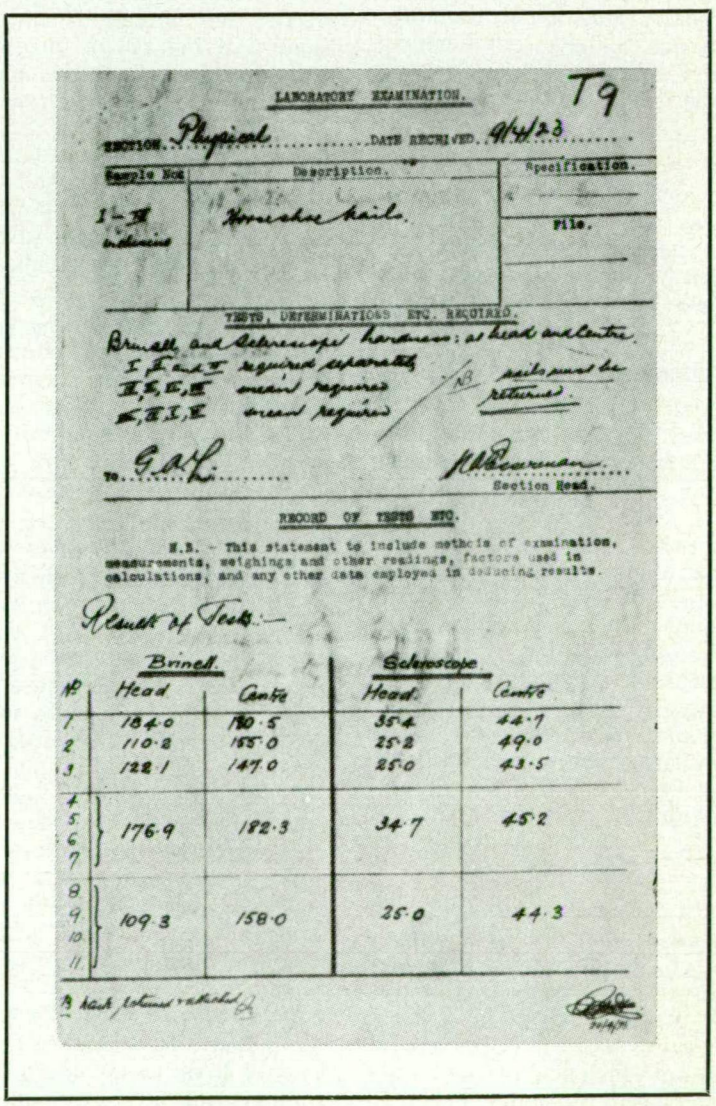
In August 1970 Mr A. R. Edwards, formerly a Superintendent at Aeronautical Research Laboratories took over as Chief Superintendent. His background of work in metallurgy, particularly with chromium alloys for gas turbines, forged an early link with DSL. Pioneered by him in the forties, the chromium alloy research later became a joint project shared by metallurgical teams from both Laboratories.

The formation of the Defence Science and Technology Organisation (DSTO) within Department of Defence in 1974 brought together a number of establishments and laboratories concerned with defence science, engineering and technology that were previously located in Departments of Air, Army, Navy and Manufacturing Industry. On 19 September 1974, DSL's increasing role in scientific studies of defence materials was recognized by a change of name to Materials Research Laboratories, and a transfer from Department of Manufacturing Industry to Department of Defence. The present staff complement of MRL is about 670, of which 205 are professionally qualified.

Synthetic polymers

Among the new materials constantly studied and appraised as substitutes for heavier and bulkier materials, are synthetic polymers. Frequently a promising polymer will fail, especially in marine or tropical environments; recently MRL won another round in this struggle. Working with several synthetic rubbers commonly used in military equipment, our chemists succeeded in covulcanizing powerful organotin fungicides into the polymer network. The new materials survived three years of assessment in temperate, tropical and marine environments, and the rubbers, in the form of 'O'-rings, were still active against fungi, and little changed mechanically. No surface of stainless steel, plastics or glass that they had contacted during the trial had suffered in any way.

This research, which should fill a need both in the defence forces and in industry, when reported at the Fourth Technology Convention, The Australian Plastics and Rubber Institute in October 1977, was awarded the inaugural Jim Smithson Medallion. This work forms part of our continuing research on organotin chemistry, an area of activity pioneered in Australia by MRL.



LABORATORY EXAMINATION. T9

SECTION. Physical ..... DATE RECEIVED. 9/4/23

Sample No.	Description.	Specification.
1–11 ordinary	Horseshoe nails.	File.

TESTS, DETERMINATIONS REQ. REQUIRED.

Brinell and Schreroscope hardness: at head and centre.
I, 2 and 3 required separately
4, 5, 6, 7 mean required
8, 9, 10, 11 mean required

nails must be returned.

To. G.A.L. ..... Section Head.

RECORD OF TESTS REQ.

N.B. - This statement to include methods of examination, measurements, weighings and other readings, factors used in calculations, and any other data employed in deducing results.

Result of Tests:—

No.	Brinell Head	Brinell Centre	Schreroscope Head	Schreroscope Centre
1	184·0	190·5	35·4	44·7
2	110·2	155·0	25·2	49·0
3	122·1	147·0	25·0	43·5
4 5 6 7	176·9	182·3	34·7	45·2
8 9 10 11	109·3	158·0	25·0	44·3

8 Mark [illegible] retained

Figure 4—From the laboratory records of 1923. Tests on horse shoe nails.

Naturally-occurring venoms

In the postwar years, as new, swift-acting lethal chemicals appeared, the need to study the mechanism of attack and to develop defences against these materials grew more urgent. Initially a medical physiologist joined the staff; since then a Group has been built up. As well as looking into the derangement of enzyme systems by chemical agents, the Group has examined a related problem, the toxins of venomous sea animals and their mode of action. One is the octopus *Hapalochlaena,* not a serious hazard to swimmers since it is not aggressive and its method of biting inefficient. But accidental bites are reported and three deaths recorded. Another, and more formidable, sea creature is the box jellyfish, believed to be responsible for many incidents of stinging and deaths. Physiology Group has examined two species, *Chironex fleckeri* and *Chiropsalmus quadrigatus,* and found their tentacle toxins to have lethal haemolytic and skin necrotizing activities. Death is due to cardiac failure.

Study of the venoms and their physiological action will lead to improved prophylaxis and treatment; as well, the range of techniques stemming from this work has been helpful in identifying other unknown compounds of this type.

Laser research noteworthy

Our contribution to laser research has been noteworthy, particularly in the light of the Group's slender resources compared with those of research teams overseas. Here the main work is with a carbon dioxide gas laser of high efficiency, around 15%, operating at a wavelength of 10.6 microns where attenuation by the atmosphere is low. Our aim—to increase the operating pressure, normally 0.1 atmospheres, so reducing the size of the device, and to eliminate, or at least reduce, the amount of expensive helium in the gas mixture—has met with success: a simple compact laser that can be scaled up to high powers.

A quasi-continuous laser of this type with a main discharge volume power of 30 kW at an efficiency of 2 litres has produced an output of 0.3 atmospheres. With resonator pressures as high as 0.5 atmospheres an efficiency of 10% has been achieved. A major factor in this success has been MRL's technique of plasma injection, which provides a background level of ionization throughout the working region of the laser under a wide range of experimental conditions, and maintains a stable and uniform electric discharge.

Even a modest laser programme means a fairly large investment; where is the return? As many countries study lasers for many reasons, the effect on materials of these new power sources becomes important. Over the years MRL has gained an accurate and detailed knowledge of how materials respond to heat and cold, to climates and marine immersion, even to explosives and shrapnel. In a time of new materials, new energy sources bring with them new problems; on the test bench of the future the laser will be an important tool.

THE WAY AHEAD

This hasty skim through MRL's history has merely touched on a small fraction of the projects that have exercised the minds and hands of scientists in many disciplines over many years. What then of the future? Where does it lie? Extrapolation is risky, crystal spheres are ever cloudy, but some small breaks in the clouds give us a glimpse of the journey ahead.

Defence, like the poor, we have always with us but the tools of defence grow more sophisticated and more expensive. To aggravate the cost burden, often their useful life grows shorter. But there may be another way out of this maze of cost spiralling and obsolescence.

Australia's Chief Defence Scientist has behind him a pool of scientists and engineers, among them staff at MRL, people in touch with the defence scene, who can assess the life and capability of equipment. People who can reassure service chiefs that an airframe is sound for five years more but weapons or instruments need updating; that a tank needs a technical face lift; or that parachutes near the end of their specified life are still dependable. A few years' extra life from expensive hardware without sacrificing efficiency could help to reduce rocketing defence expenditure.

Toxic wastes: an old problem

As industry accelerates, the problems of toxic wastes loom large; so another area where our talents and instruments will be in greater demand—already they have been called on—is in controlling pollution. Not that this is new. R. E. Summers remembers a task of the 1920s when A. E. Leighton asked MSL to analyse the river water above and below his Cordite Factory to ensure he would not be blamed for any pollution in the Maribyrnong. MRL has supervised waste treatment installations in Government factories at Lithgow, Fisherman's Bend, Footscray and Maribyrnong and at Bendigo where the work is not yet completed.

Birds flock to a cleansed river

Formerly, untreated wastes poured into the Maribyrnong River; now that the MRL processes have stemmed this noxious flow, the river has come to life again. Seagulls abound, and the return of cormorants and often herons, egrets and spoonbills is an enchanting proof of the worth of the treatment.

Another Group, aware of the urgent need to conserve our marine environment, will be keeping close watch on the impact of dockyards and naval ships. Frequently harbours are sited in estuaries, well known as productive and sensitive ecosystems, many of them already sorely stressed. Only careful husbandry guided by scientific study will ensure the sea remains a living resource for man rather than just a dump for his garbage.

Guarding the web of life

The web of life, resilient and fecund, yet has its fragile strands. Where these are over-stretched they must be relieved and reinforced lest the whole structure collapse, for the task of rebuilding might be beyond our strength and skill. Materials Research Laboratories with its expertise in fields such as physical, organic and polymer chemistry, metallurgy, physics, mathematics, pharmacology, physiology and biochemistry will continue to play a role with further research and development activity on a wide range of materials of interest to us all.

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APPLIED RESEARCH

ON

ORGANOMETALLICS AND ORGANIC MATERIALS

APPLIED RESEARCH ON ORGANOMETALLICS AND ORGANIC MATERIALS

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MELBOURNE
AUSTRALIA

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D.Sc THESIS

"Applied Research on Organometallics and Organic Materials"

by P. DUNN

Errata

Page 59, Para. 4. 1955 should read 1956

66, Reference 1. Replace 12 by No. 12.

4.40 (Appendix 4C). Add Appendix 4C

4.41 (Appendix 4C), line 6. Replace "assessed and compared with" by "distilled at".

(P. DUNN)
13 March 1980

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PREFACE

This thesis submitted for the degree of Doctor of Science, University of Tasmania, is entitled "Applied Research on Organometallics and Organic Materials". It represents work undertaken in the employment of the Commonwealth of Australia during the period 1951-78. The thesis resulted from a suggestion that some early work carried out by the author on compounds based on phosphorus, silicon and tin could still be of interest to scientists associated with organometallic chemistry. The approval for the unlimited public release of some of this work has enabled it now to be included.

Prior to joining Defence Standards Laboratories, Department of Supply (now Materials Research Laboratories, Department of Defence) early in 1951, studies for the Degrees of Bachelor of Science and Bachelor of Science with Honours were undertaken at the University of Tasmania. A short period of post graduate research at the University followed the completion of the academic requirements for an Honours Degree.

At the Ministry of Supply, Britain,during 1951-53,work was undertaken on special organometallic compounds. The synthesis of a new series of ether-containing organophosphorus compounds was initiated in collaboration with the late *A.H. FORD-MOORE*, a specialist in organophosphorus chemistry. This was followed, at my suggestion, by a detailed study of the structure-toxicity relationships of some silicon analogues of the organophosphorus compounds. In the early 1950's, the chemistry of organosilicon compounds was at an early stage of development and this area of research was relatively unexplored.

The interest generated in phosphorus and silicon chemistry in Britain stimulated further research on organometallics (and related materials) following my return to Australia. One of these activities was the synthesis of a new series of tetraorthoesters of titanium as these materials were of interest as vehicles for heat-resistant paints. This work was completed in 1957.

At about the same period, the author became involved with scientific studies associated with several atomic tests conducted at Maralinga, South Australia, and code named *Operation BUFFALO*.

A further area of research on organometallics was initiated in 1957 and this work, on the chemistry and applications of organotin compounds, has continued for twenty years. During this period, other scientists at MRL have also been associated with some of the research activities.

In the mid-1960's, during a period of secondment to the US Army, work was initiated on the development of high performance, non-black, ethylene-propylene diene elastomers, using new synthetic materials that had been introduced in the USA, during 1963-64. On return to Australia, applied research on organotin compounds was continued as well as work on a wide range of organic materials, mainly rubbers and plastics. These types of activities are still in progress.

The original aim of our research activities on organometallics was to find new applications for these interesting and versatile chemicals. In the role of additives they have shown considerable promise in the modification of the properties of a wide range of organic materials such as: rubbers; plastics; adhesives; sealants; coatings; and fibres. In this thesis details are given of our efforts to modify organic materials by the addition of organometallic compounds. To record my continuing interest in applied research, other items associated with organic analyses and organic materials are included.

During the period 1951-74, the research was undertaken at Defence Standards Laboratories (DSL), first in Department of Supply and then in Department of Manufacturing Industry. On 19 September 1974, DSL's increasing role in scientific studies of defence materials was recognised by a change of name to Materials Research Laboratories (MRL) and the transfer of MRL from Department of Manufacturing Industry to Department of Defence. Summary details of research activities during the period 1951-78, are given at Appendix 1.

The work reported in this thesis was initiated by the author and undertaken, either alone or, with the collaboration of other scientific staff. Where appropriate, results have been published in the open scientific literature or in the form of Government reports, with collaboration being recognised by co-authorship. Details of co-authors, including their past and present designations and present positions, are given at Appendix 2.

Although the research described was conducted over a number of years, it has all been concerned with the understanding of unexpected chemical phenomena and the development of new and improved organic materials of primary interest to the Defence Force of Australia as well as to the scientific community in general.

All the work reported in this thesis is original and is now unclassified. Some previously unpublished work is also included. The nature of this work is indicated in the text, together with details of official references to documents available from Materials Research Laboratories. To confirm the initiation of, and participation in, the reported research activities, copies of some specific documentation relating to the work presented are also included.

It is a pleasure to record that the late *Arthur FORD-MOORE*, Chemical Defence Establishment, Ministry of Defence, Porton, Britain, was responsible for the stimulation of my interest in defence science in general, and organometallic chemistry in particular. The example of his aptitude towards the solving of chemical problems, his manipulative skill in the laboratory and his general philosophy to research, provided the stimulus that was necessary to maintain a long-term continuing interest in organometallics and organic materials of defence interest.

None of the work presented in this thesis has previously been submitted for the Degree of Doctor of Science.

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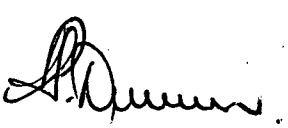

(P. DUNN)
24 January, 1979

AUTHOR'S NOTE - LAYOUT OF THESIS

The format of this thesis consists of a *review of work undertaken*, together with *Appendices* based on journal publications, Government reports and some previously unpublished information. Where necessary, the status of the work included is indicated on the cover page of each Appendix.

The work reported is divided into *three* major parts, namely:

Part I is concerned with work on the *chemistry of organometallic compounds* based on phosphorus, silicon and tin. The major contribution has been concerned with organotin chemistry. For convenience, research activities related to tetraorthoesters of titanium are also included.

Part II describes *applied research activities on organic materials*, particularly the stress cracking of polyamides (nylons) and the development of improved materials based on synthetic polymers.

Part III reports work undertaken on the *detection and identification* in the thyroid of animals, of radioactive isotopes formed from an atomic explosion. Also presented, in summary form, is information on some *miscellaneous supporting research activities*, including the instrumental analysis of organic materials. Some review articles are also included.

Journal articles are presented complete and Government reports mainly in the form of abstracts. Minor editorial corrections have been made to unpublished work in order to conform to the general style of the thesis. The format of each paper, the style of the references and the system of units used, remains unchanged. Original documents are available for examination. Appendices 3 and 4 have been retyped as the original format of each publication was on foolscap. For convenience, Appendices are listed in *numerical sequence* with each being *individually sub-numbered*.

Photographs of items of scientific or historical interest, or of cover or title pages of documents out of print or in short supply, are included. An *index* to the review is also included.

SUMMARY

This thesis presents details of *unclassified* applied research activities undertaken by the author (and colleagues) during the period 1951-78. Most of the work was carried out in the Organic Chemistry Division, Materials Research Laboratories, Defence Science and Technology Organisation, Department of Defence, Melbourne, Australia. The remainder was undertaken during periods of secondment to defence research laboratories in Britain and the United States of America.

The major aspects of the work described in the *three* parts of the thesis, are:

1. PART I. ORGANOMETALLICS

1.1 A new series of ether-containing organophosphorus compounds was prepared and an assessment made of the toxicity-structure relationships of the compounds.

1.2 The silicon analogues of a number of organophosphorus compounds were synthesized and their physiological activity assessed.

1.3 New mixed tetraorthoesters of titanium were prepared and converted into polymeric compounds, by the technique of partial hydrolysis, using water in butanol.

1.4 Reactions between ammonia or pyridine and titanium alkoxides or chlorotitanium alkoxides were investigated. The inter-relationship of the different types of titanium addition compounds was established.

1.5 The chemistry of organotin compounds was initiated in Australia. Following preliminary toxicological assessment of compounds of interest, work was undertaken on the use of organotin compounds, including polymeric organotin esters, as fungicides for rubbers and plastics. A large number of new organotin compounds was synthesized, including tributyltin fluoride. This latter compound has now achieved considerable commercial significance. A detailed survey of the infrared spectra of organotin compounds was undertaken. Spectral data were used for structural studies of organotin carboxylates and a number of nitrogen-containing organotin compounds. Detailed structural and chemical studies were also undertaken on tributyltin fluoride, in particular the formation of co-ordinated polymers in solution in certain

solvents. To utilize organotin compounds in new and novel applications, investigations were undertaken to determine their potential as antifouling compounds, impregnants for timber, fungicides for rubbers and fungicides and stabilizers for plasticised poly(vinyl chloride) plastics.

2. PART II. APPLIED RESEARCH ON ORGANIC MATERIALS

2.1 The stress-cracking of polyamide plastics (nylons) by metal salts was reported and studies undertaken on the mode of failure of components and on the mechanism of stress cracking. A new simple technique for the study of the stress cracking of nylon films was developed. Improvements in the adhesive bonding of nylon, resulting from etching of the surface by stress-cracking agents, were investigated.

2.2 The need for new high performance seals for nylon components resulted in the development of peroxide-cured, ethylene-propylene copolymer vulcanizates and their initial introduction into Australia.

2.3 Detailed studies were undertaken on the development of silica-reinforced,ethylene-propylene terpolymer vulcanizates. Special compounds produced as part of a long-term ageing programme have been found to retain excellent mechanical properties after storage for over fourteen years.

2.4 Studies have shown that ethylene-propylene terpolymer vulcanizates have good resistance to weathering under severe environmental conditions in tropical Australia. Compounds of known composition can now be recommended for service in adverse environments.

2.5 As a result of a collaborative study with local industry, magnetic rubbers, based on Australian-produced ferrites, were developed.

2.6 In studies on the underwater protection of timber, unusual imprints of barnacles on a particular synthetic rubber coating were observed. The nature of these imprints, in relation to the growth of the barnacle, was investigated.

2.7 Small scale tests for smoke generation and flammability have been used to identify potentially hazardous materials that might be used in naval vessels. Work is now required to adequately assess all the factors associated with the ignition and combustion of organic materials of interest to the Defence Force.

2.8 Miscellaneous research and development activities associated with organic materials have included studies on: direct moulded soles for combat footwear; rubber target facings; rubber plugs for detonantless fuzes; and the assessment of weathering of polyolefins under Australian conditions.

3. PART III. GENERAL SUPPORTING RESEARCH ACTIVITIES

3.1 As part of a series of atomic trials undertaken in Australia, the extent to which different isotopes of iodine contributed to the dose in the thyroid of grazing animals shortly after detonation, was examined.

3.2 In collaboration with others, techniques were developed for the determination of pentachlorophenyl laurate in fungicidal compositions and the analysis of icing inhibitors based on ethylene glycol monomethyl ether in fuels. The decomposition of poly(vinyl chloride) used in rocket motor insulants was investigated by the application of thermal analytical methods.

3.3 The technique of thermal analysis was also used in studies on the melting of polyacrylonitrile and the identification of acrylic fibres.

3.4 A rapid and simple technique was developed for the identification of transparent materials, mostly plastics, used in safety applications.

3.5 Because of the need to disseminate details of the scope and application of research work, reviews have been published on topics such as: plastics and metals; on organic materials (mainly polymers) in adverse environments; and on fire hazards of plastics materials.

The thesis contains reprints, abstracts and copies of research submissions and associated documentation related to the work described.

ACKNOWLEDGEMENTS

As with most applied research activities, much of the work reported in this thesis has been generated over many years with the assistance of dedicated support staff. Their assistance is acknowledged, particularly those technical staff whose skills have been exercised in seeking information related to the reported programmes.

The efforts provided by scientific staff has been acknowledged in the reporting of particular programmes. Their contributions in the specialized fields of scanning electron microscopy, radiography, technical photography, instrumental and chemical analysis, mechanical testing and mycological assessment, is further acknowledged. The collaboration of particular scientific staff directly associated with the reported work, is acknowledged by co-authorship.

I thank all my co-workers whose names appear throughout this thesis, and without whose efforts and interest the research undertaken on organometallics and organic materials could not have been accomplished.

As no research and development activity is complete until the work has been adequately reported, the efforts of all the steno-secretaries and typists who have struggled with the production of draft and final manuscripts, is gratefully acknowledged.

The opportunity to undertake within the Departments of Supply, Manufacturing Industry and Defence, Commonwealth of Australia, the type of applied research reported in this thesis, is also acknowledged.

1. INTRODUCTION

The aim of this thesis is to present details of applied research activities undertaken over a period of some years. The thesis consists of a review of these activities together with a compilation of published work, either in the form of reprints, copies of government reports, xerox copies of items hard to obtain or out-of-print and photocopies of items and figures of particular interest. The review is not intended to be all-embracing, but rather to indicate the objective of the research undertaken, its relationship to major programmes, the significance of the results obtained and the influence of the results on subsequent research activities in various laboratories.

For convenience the thesis is divided into three major parts, each essentially self contained, but inter-related because of the nature of the work reported and the types of materials involved. Leading references only are listed in the review. Comprehensive references are listed in the papers in the Appendices and these should be read in conjunction with the leading references.

The work presented has been undertaken by the author while employed by the Commonwealth of Australia, either in Australia or during periods of secondment to overseas defence research establishments. Details are given at Appendix 1. In Australia, the work was undertaken in the Organic Chemistry Division, Materials Research Laboratories (MRL), Department of Defence. The history of MRL has recently been reported by Gleeson (1) and summary details of current activities of the Division are also available (2).

PART I. ORGANOMETALLICS

2. ORGANOPHOSPHORUS COMPOUNDS

In the late 1930's, Dr Gerhard Schrader was involved in a research study on the synthesis of new organophosphorus compounds that could have potential for use as insecticides. The research, undertaken at the Leverkusen Laboratories of I.G. Farbenindustrie, Germany, resulted in the discovery of compounds with unexpectedly high mammalian toxicity. The development of a number of these compounds was undertaken in great secrecy during World War II, and details of the chemistry and production were not known to the Allies until near the end of the war. Three new compounds attracted particular attention, namely, *Tabun* (GA: ethyl N,N-dimethyl-phosphoroamidocyanidate), *Sarin* (GB: isopropyl methylphosphonoflucridate)

and,in 1944, *Soman* (GD: 1,2,2-trimethylpropyl methylphosphonofluoridate). These nerve agents were colourless, odourless and highly toxic liquids.

Nerve agents act on the body by interfering with the chemical reactions in nerves that control muscles. In particular, they inhibit the action of cholinesterase (thus being known as anticholinesterases) and this results in a build-up of acetylcholine in muscles. Coordinated action in the muscles is impaired and causes serious interruption of vital body functions. In comparison to other chemicals, even small quantities of nerve agent, either inhaled or absorbed through the skin, can rapidly be fatal.

The discovery of the nerve agents in Germany, stimulated and then accelerated investigations in Britain and the USA, mainly during the period mid-1940's to early 1960's. Areas of particular interest included: chemistry of organophosphorus compounds, assessment of physical properties, determination of structure-toxicity relationships, and investigations concerned with detection, mode of action on man, therapy, stability and decontamination. Much of the work was classified, but gradually over a number of years reliable reports on the toxic organophosphorus compounds have been issued.

The basic chemistry of the organophosphorus compounds was reported by Kosolapoff (3) in 1950, while, in 1957, Saunders (4) described some aspects of the chemistry and toxic action of organic compounds of phosphorus and fluorine. Heath (5), in a comprehensive book on organophosphorus poisons, reported on the mode and action of many anticholinesterases and related compounds.

The military implications of the nerve agents, their production by the Germans during World War II, and the reasons for their non-use during that conflict, have been discussed by Rothschild (6). Clarke (7) has produced a book that provides a good general account of the chemical and biological aspects of weaponry, in particular the developments that occurred during World War II that could have a military impact in future conflicts. The bibliography includes a number of papers of general interest. The early use of chemicals in military applications and those now available that is, lethal agents, incapacitating agents and harassing (riot control) agents, has been reviewed by Robinson (8).

In recent years, the United Nations and other international organisations have produced authoritative reports (9-13) on chemical and biological agents, including data on chemical, physical and toxicological

properties. Meselson (13), in particular, has discussed the use of chemical weapons in a future conflict, and reviewed possible measures for limiting or eliminating chemical warfare forces. Early in 1978, Lepkowski (14) published a special account on chemical warfare, including details of the structure of particular compounds and the extent of stockpiles of agents held by major powers.

An area of particular concern in the early 1950's, was the relationship between chemical structure and toxicity of certain organophosphorus compounds. Hudson (15), in 1965, reported detailed studies in this field. In 1970, when The Chemical Society, London (16) introduced their literature reviews on organophosphorus chemistry, further work on the subject was reported.

This brief review of unclassified work on toxic organophosphorus chemistry, highlights some of the reasons why, during the 1945-1960 period, active research on the subject was initiated. Some of the work undertaken by the author on organophosphorus compounds has been released for public disclosure, and can now be presented.

In conjunction with the late A.H. FORD-MOORE, the work reported at Appendix 3(a and b) (17) was undertaken at the Chemical Defence Experimental Establishment, Ministry of Supply, Porton, Britain. The compound of primary interest at that time was *Sarin*, isopropyl methylfluorophosphonite. The present nomenclature for this compound is isopropyl methylphosphonofluoridate (10,p.35). Any alteration of the alkane (methyl) part of the *Sarin* molecule resulted in a considerable reduction in toxicity. It was of interest, therefore, to assess what effect substitution of the methyl group by a group containing an ether linkage would have on toxicity.

Using special techniques designed to enable highly toxic materials to be handled safely, four members of a new type of fluorophosphonite, having an ether group attached to the phosphorus atom, were prepared. Details are given at Appendix 3b. In this synthesis it was necessary to fluorinate isopropyl alkoxyalkylchlorophosphonites, compounds which were very resistant to fluorination using conventional agents such as antimony trifluoride. We found ammonium fluoride to be an excellent fluorinating agent for certain organometallic compounds, and this observation had a significant effect on later work associated with organotin fluorides.

Toxicity data (relative molar toxicity compared to *Sarin*), showed that there was a marked reduction in toxicity by replacement of the methyl group by an ether group. The extent of the reduction was related to the acidic nature of the particular ether substituent.

This investigation formed part of a comprehensive study by others of structure - toxicity relationships on a large number of organophosphorus compounds. The results of the present work were utilized in the development of therapy against organophosphorus poisons, such as that described by Heath (5).

3. ORGANOSILICON COMPOUNDS

Because of the powerful physiological activity of many organophosphorus compounds, it was of interest to study compounds with similar structures but containing a metal atom different to phosphorus. The organometallic compounds selected for further study were those based on silicon.

In 1937, Kipping (18) proposed that the chemistry of organosilicon compounds was different from classical organic chemistry. Using his traditional work as a starting point, researchers in the early 1940's developed new classes of organosilicon polymers ranging from viscous fluids and soft, putty-like products to hard resinous materials. Burkhard et al (19) presented a complete bibliography of the Kipping papers and also a review of the state of organosilicon chemistry around 1947. The reports of Post (20), Rochow (21, 22), McGregor (23) and Rochow, Hurd and Lewis (24) describe the state of organosilicon chemistry in the early 1950's.

Although a considerable number of organosilicon compounds had been reported by 1952, very little information was available on their toxicological properties. Rochow (21, p.157) concluded that, "silicon does not cause poisoning of the type experienced with heavy metals and that the organosilicon compounds so far encountered do not seem to be toxic in themselves". Because of the unique physiological properties of specific chemical structures associated with organophosphorus compounds, it was considered prudent to undertake a detailed study of certain classes of organosilicon compounds. The work,which was undertaken during 1952-53, has not been previously reported in the open literature.

Details of a study of the silicon analogues of some organophosphorus compounds are given at Appendix 4(a and b) (25). In order to make an arbitrary comparison of the structure of various organosilicon and organophosphorus compounds, the Si-R group and the P=O group were considered to be structurally equivalent. Thus the silicon equivalent of the extremely toxic isopropyl methylphosphonofluoridate, *Sarin*, was $CH_3(R)SiF(OPr)$,isopropoxymethylalkylfluorosilane. Using this system, many organosilicon compounds (including twenty three new products) were prepared and physiologically assayed. The main types investigated were:

alkylalkoxychloro- and fluorosilanes, alkoxydialkylaminoalkylchlorosilanes, alkyl- and alkoxydialkylaminosilanes and alkylalkoxydisiloxanes and disilazanes. As part of this work the efficient method of fluorinating chloro-organosilicon compounds using anhydrous ammonium fluoride (Appendix 4b, p.4.6) was developed from the original work of Wilkins (26).

Comprehensive details of the chemistry, structure, experimental methods and properties of a large number of organosilicon compounds are given at Appendix 4b. Of particular interest was the work conducted on alkylalkoxydisilazanes (Appendix 4b, p.4.13) using a modification of the method of Rosnati (27). The silazane bond, Si-N-Si, is very stable and resistant to attack by boiling water or dilute alkali. Kirk and Othmer (28) reported on the properties of similar compounds in 1954.

Details of the toxicological assessments including, in particular, the insecticidal activity of new compounds are given at Appendix 4b (p.4.16). Results confirmed that although many of the organosilicon compounds had structures simulating some of the most toxic phosphorus compounds known, the silicon molecule itself appeared to possess little, if any, intrinsic toxicological activity. Replacement of the P=O group in the toxic organophosphorus compounds by the Si-R group, markedly reduced the toxicity of the former compounds. The observed low toxicity of the silicon analogues of the organophosphorus compounds that were prepared and tested, did not therefore give great hope of finding physiologically active compounds.

These general conclusions were confirmed by a further study on the toxicological properties of some methylisocyanosilanes (Appendix 4c, p.4.40), particularly dimethyldiisocyanosilane. This compound, prepared by the reaction of silver cyanide on dimethyldibromosilane, was assessed for toxicity and the toxicity shown to relate to contained cyanide, the latter being liberated as hydrogen cyanide by reaction with moisture. The result was not unexpected and confirmed similar results obtained on silicon compounds containing 2-fluoroethoxy and p-nitrophenoxy groups.

This detailed study on organosilicon compounds suggested that it was unlikely that significant physiological activity was inherent in the types of structures investigated. It was therefore considered remote that organosilicon compounds would find commercial use in applications such as insecticides, fungicides, bactericides and rodenticides. Subsequent extensive research and evaluation undertaken in many laboratories during the past 25 years, has shown this early prediction to be correct.

4. TETRAORTHOESTERS OF TITANIUM

Although not strictly organometallic compounds, in that they do not contain a carbon to metal atom bond, research undertaken at MRL on tetraorthoesters of titanium has been included in this part of the thesis, as a matter of convenience.

In the early 1940's, Post (29) described current research being conducted on a number of aliphatic orthoesters, including those based on titanium. Kraitzer, McTaggert and Winter (30, 31) at MRL, in 1947, reported the development of an aluminium-pigmented butyl titanate (tetrabutoxy titanium), heat-resisting paint suitable for the protection of steel against high temperature corrosion up to 600°C. Development work continued at MRL and, in 1953, Winter (32) reported on the preparation of polymeric butyl titanates, their hydrolysis and film-forming properties, as well as the formulation and performance of butyl titanate paints. As part of this general programme, Winter (33) also studied the use of water in the reaction with titanium esters to form, in the first instance, hydroxy compounds which then condensed to form polymeric products. A brief review summarising work on organic titanates was published, in 1954, by Blair et al (34).

As part of the author's activities, a research programme was initiated, the aim of which was to study the preparation and polymerization of mixed tetraorthoesters of titanium. As reported at Appendix 5a (35), a method, based on the stepwise reaction of different alcohols with titanium tetrachloride and the use of ammonia to remove liberated hydrogen chloride, was developed for the synthesis of mixed methyl butyl esters of titanium. Using this technique, titanium monomethoxide tri-n-butoxide, titanium dimethoxide di-n-butoxide and titanium trimethoxide mono-n-butoxide were prepared and characterized. In this work, a spectrophotometric method was developed for the estimation of methoxyl using a modification of the technique described by Mathers and Pro (36). Studies were also undertaken on the polymerization of monomeric mixed methyl butyl esters of titanium, using varying amounts of water dissolved in butanol. As a result of these studies at MRL, several methoxy butoxy polytitanoxanes were examined, by others, for their film-forming properties and suitability for use as paint vehicles.

Bischoff and Adkins (37) first reported the preparation of titanium tetramethoxide by the reaction of sodium methylate with titanium tetrachloride. Teichner (38) prepared a similar compound from titanium

tetrachloride, methanol and ammonia. In work at MRL, the method was modified to give improved yields of titanium tetramethoxide (Appendix 5a, p.462). Recrystallization from toluene at $-5^{o}C$, gave transparent crystals with a slight yellowish tint that were shown to have adequate resistance to hydrolysis when stored under appropriate conditions.

In the early 1960's, Ibers (39) reported on the crystal structure of titanium tetraethoxide and Witters and Caughlan (40) studied the structure of titanium monomethoxide triethoxide. The local availability of titanium tetramethoxide enabled Wright and Williams (41), at MRL about 1967, to undertake a detailed study of the crystal and molecular structure of the compound. Their work showed that titanium tetramethoxide, $Ti(OCH_3)_4$, crystallized in the triclinic space group, and consisted of discrete tetrameric molecules, $Ti_4(OCH_3)_{16}$. Detailed spatial dimensions of the crystalline lattice were assigned. A sample of titanium tetramethoxide used in this study and stored continuously in a desiccator over silica gel, had a unchanged m.p. of $217^{o}C$ when re-examined in 1977.

As part of studies undertaken on the preparation and polymerization of mixed titanium tetraorthoesters, some unusual reactions were observed when ammonia was used as a dehydrochlorinating agent. This resulted in further investigations of the reaction of titanium tetrachloride, chlorotitanium alkoxides and titanium tetraalkoxides with ammonia and pyridine. Details are given at Appendix 5b (42).

With ammonia and pyridine, organotitanium compounds form solid, stable, addition complexes and these can react further with alcohols to give fully substituted orthoesters. In some of the ammonia complexes, titanium exhibited covalencies of five and six. Compounds prepared and evaluated included: titanium tetrachloride tetra-ammoniate and hexa-ammoniate, trichlorotitanium monobutoxide tri-ammoniate and penta-ammoniate, monochlorotitanium tributoxide mono-ammoniate and tri-ammoniate, titanium tetrabutoxide mono-ammoniate, titanium tetrachloride dipyridinate, trichlorotitanium monobutoxide tripyridinate and monochlorotitanium tributoxide monopyridinate.

The effect of heat and vacuum conditions on the ammonia and pyridine complexes, and their reactions with methanol and butanol was examined. This investigation enabled the inter-relationship of the various complexes to be established (Appendix 5b, p.226), and contributed to an understanding of the formation of mixed titanium tetraalkoxides by traditional routes (30, 31, 35).

5. ORGANOTIN COMPOUNDS

5.1 Commencement of Activities

During 1957, the author was required to initiate research and development activities on rubbers, plastics and adhesives of defence interest. With a background in organic synthesis and organometallic chemistry it was appropriate to incorporate these areas of interest into the new activities.

Experience in World War II had shown that enormous losses of materiel occurred in the tropical regions as a result of biological attack, in particular by fungi and insects and, to a lesser extent, rodents. A proposed area of interesting research concerned means of improving the long-term resistance to degradation of organic materials to biological attack, both while in storage and in use.

Because of a continuing interest in the chemistry of phosphorus, silicon and titanium, the work of Luijten and van der Kerk (43, 44) in the mid-1950's attracted particular attention. These workers had identified the significant fungicidal activity of the trialkyl and triaryl organotin compounds. Practical applications were being sought and we believed that there was considerable scope for the use of organotin compounds as fungicides for a wide range of organic materials, particularly rubbers and plastics. This aspect formed the primary objective of a modest research programme which has continued for two decades. The main aims were:

(i) Synthesis of new organotin compounds of research interest.

(ii) Investigation of the properties of selected organotin compounds.

(iii) Utilization of organotin compounds as additives for rubbers, plastics and adhesives in order to modify and improve their service characteristics.

5.2 Initial Surveys

About 1957, research on the chemistry of organotin compounds was just beginning to develop. Since that time it has attracted active interest in many countries. At the recent Second International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead, Smith (45) showed that industrial consumption of organotin chemicals had increased dramatically during the last decade and that the annual consumption in 1977 was close to 30 000 tonnes. New applications are continually being discovered, particularly as organotins have a favourable reputation in relation to current environmental requirements.

Recently, the chemistry and applications of organotin compounds have been well documented in a number of reference publications. Those of particular interest in relation to the present work are Tin and Its Uses (46) and the books or reviews by Ingham, Rosenberg and Gilman (47), Stone and West (48), Dub (49), Poller (50), Sawyer (51), Abel and Stone (52), Gielen (53) and Zuckerman (54).

Prior to the commencement of experimental work at MRL, a survey was undertaken on the possible potential of organotin polymers. Examination of laboratory records showed that the author initiated the first proposals for work on organotin compounds in August, 1958. A xerox copy of the original minute is given at Appendix 6a, and a retyped copy of the submission on organotin polymers at Appendix 6b. This original survey was further extended in October, 1958 (Appendix 6c). It is appropriate to submit these survey documents in this review as they indicate the initial thoughts, suggestions and plans that existed in 1958 and they provided the basis for our continuing research effort on organotin compounds. Of particular interest are the sections on organotin halides (Appendix 6b, p. 6.6), toxicity (Appendix 6c, p. 6.15), organotin fluorides (Appendix 6c, p. 6.16), new organotin polymers (Appendix 6c, 6.16), and general discussion (Appendix 6c, p. 6.18).

5.3 Toxicity of Organotin Compounds

Prior to the commencement of a large-scale programme on the synthesis, handling and evaluation of organotin compounds as additives for organic materials, it was necessary to determine the extent of any physiological activity. Previous experience with organophosphorus compounds (Section 2) had stressed the need to be confident that new organometallic compounds did not possess any unexpectedly high mammalian toxicity.

Lyle (55) had studied the effects of butyltin compounds on process workers and showed that although most organotin compounds were harmless, some specific alkyl compounds were soluble in body fluids and toxic. The diethyl and triethyl organotins were reported to be the most toxic, while the corresponding octyl compounds were claimed by Luijten and Pezarra (56) to be non-toxic.

In 1958, some organotin acetates and fluorides were prepared by the author and submitted to Physiology Group, MRL for assessment of toxicities. Triethyltin fluoride, tributyltin acetate and fluoride and triphenyltin acetate and fluoride were assayed and probable MLD100 (mg/kg) values determined using rats as test animals. These organotin compounds were selected for evaluation as they were typical of some of the alkyl and

aryl compounds on which investigations were proposed. Also the introduction of the fluoride group might have increased the physiological activity of the molecule and this would identify compounds that might require special techniques in handling.

The results of these original assessments, which we believe were the first on organotin compounds to be undertaken in Australia, are given at Appendix 7. Active physiological response was not observed with any of the test compounds. The results indicated that, provided normal care with handling was exercised in the laboratory, organotin compounds were relatively safe materials and unusual problems were unlikely. Because of the reported dermatitic nature of certain organotin compounds, care was required in order to prevent unnecessary skin contact.

During the last few years, extensive research has been undertaken on the toxicological and environmental performance of organotin compounds. Barnes and Stoner (57), Ascher and Nissim (58) and Barnes (59) have published extensive reviews on the subject. Poller (50, p. 271) has published a chapter on biological effects and consequent applications of organotin compounds, including data on acute toxicities of some trialkyl and triaryltin compounds. The applications and biological effects of organotin compounds have also been discussed, in detail, by Luijten (60).

5.4 Elastomeric and Fungicidal Organotin Compounds (including organotin polymers)

During 1961-62, research was undertaken on elastomeric and fungicidal organotin compounds as additives for rubbers and plastics. Not only were new compounds synthesized and evaluated for biocidal activity, but new and existing compounds were formulated into natural and synthetic rubbers in order that the properties of the resultant vulcanizates could be determined.

The biodegradation of organic materials has been a problem for many years and regular international reviews and symposia are held on the subject. The recent reports by Sharpley and Kaplan (61) and Walters (62) describe the present situation. At MRL, facilities are available for the evaluation of organic materials against a wide range of fungal species and the techniques used have been reported by Upsher (63). Kerner-Gang (64) has also described techniques for assessing the resistance of special products, such as rubber pipe-joint rings and sealants, to microorganisms.

In 1962, a paper was presented by the author (65) at the 36th Congress of ANZAAS, Sydney, Australia on work undertaken on elastomeric and fungicidal organotin compounds. The paper is reproduced at Appendix 8a.

The state of research on organotin polymers up to 1962 was described, and information included on work undertaken at MRL on organotin polymers based on acrylates and methacrylates, crosslinking of organotin polymers and fungicidal activity of organotin compounds.

Additional information relating to this work is given at Appendix 8b, together with details of formulations and properties of resultant vulcanizates. This latter work showed that trialkyltin compounds could be added to rubbers to provide protection against microbial attack. The use of poly(tributyltin methacrylate) or bis(tributyltin) maleate at a level of four parts per hundred of rubber in natural, styrene-butadiene and polychloroprene rubbers did not markedly affect the physical properties of the vulcanizate. With butadiene-acrylonitrile rubber, the use of bis(tributyltin) maleate had a profound effect on rate of cure. Incorporation of organotin compounds into rubber formulations did not affect the resistance of the vulcanizates to attack by ozone.

In 1972, Henry and Davidsohn (66) reviewed research activities on organotin polymers and noted the similarity of work undertaken at MRL (65) with that of Russian workers (67). Montermoso, Andrews and Marinelli (68, 69), working with the US Department of Army, Shostakovskii (70) and Dunn (65) were all conducting studies on the synthesis of poly(tributyltin acrylate) and methacrylate as well as various copolymer systems. Attempts to crosslink the polymers using conventional systems based on peroxides, amines, sulphur, metal oxides and phenolic resins were unsuccessful (Appendix 8a).

An interesting extension of this work was the development of a method for the polymerization of tributyltin methacrylate or acrylate in solution in a plasticiser carrier such as dinonyl phthalate (Appendix 8a, p. 8.9). Poly(tributyltin methacrylate) as a 25-33 percent by weight, solution in plasticiser was a transparent, viscous liquid that could readily be incorporated into rubber and plastics formulations. Evaluation of the polymer in polychloroprene rubber, butadiene-acrylonitrile rubber, styrene-butadiene rubber, natural rubber and plasticised poly(vinyl chloride) (Appendix 8a, p. 8.18 - 8.19) showed the organotin materials inhibited the growth of a number of fungal strains in controlled laboratory experiments.

In work undertaken in the early 1970's, by others at MRL, on the use of rubber as an antifouling material, some of the formulations used in the present work formed the basis of the research programme. This later work, together with out work in the early 1960's, showed that when high levels of organotin compounds (usually about 10% by weight, or greater), were incorporated into rubbers, serious retardation of sulphur-based curing systems occurred. This observation led to the development of a new and novel system for the incorporation of high levels of organotin compounds into peroxide-cured rubber vulcanizates (Section 5.9).

As described previously (65), poly(tributyltin methacrylate) could be prepared by the use of thermal means, by peroxides or by emulsion polymerization techniques (Appendix 8a, p. 8.15). As part of studies on this system, the preparation of copolymers of tributyltin methacrylate and chloroethyl vinyl ether was investigated using both emulsion and peroxide polymerization techniques. The objective of the work was to prepare a copolymer containing a chlorine atom pendant to the main vinyl backbone chain in order that crosslinking might be effected via the pendant chlorine. Details of the work are given at Appendix 8c (8.27).

Analytical results indicated that chloroethyl vinyl ether could be copolymerized into the polymer. The effect of type of peroxide, content of peroxide and content of chloroethyl vinyl ether on copolymerization, was investigated. As attempts to crosslink interesting copolymers to form useful products were not successful, the work was terminated. However, the copolymer based on tributyltin methacrylate and chloroethyl vinyl ether in the ratio 90:10 and polymerized using 1% by weight, of benzoyl peroxide could warrant further investigation.

5.5 Synthesis of New Organotin Compounds

In the early 1960's, the author, with the experimental assistance of T. NORRIS, embarked on an extensive synthetic programme, the aim of which was to prepare new compounds of interest as well as certain reported compounds that were required for further evaluation. The reviews of Ingham, Rosenberg and Gilman (47), Neumann (71), Luijten and van der Kerk (44) and Noltes and van der Kerk (72) indicated that at that time well over 800 organotin compounds had been synthesized and many of them described in detail.

Appendix 9a (73) describes in detail the synthesis of trialkyltin carboxylates (Section 2.1), bis(tributyltin) carboxylates (Section 2.2), miscellaneous organotin carboxylates (Section 2.3), organotin oxides and hydroxides (Section 2.4), organotin hydrides (Section

2.5) organotin halides (Section 2.6), and organotin compounds containing nitrogen (Section 2.7). As the original report (73) is now out-of-print, the report is reproduced in full. As part of the work, analytical procedures were developed for the characterization of certain organotin compounds. About sixty new organotin compounds were prepared, and many of these were used in studies on infrared spectral characteristics (Section 5.6).

The synthetic programme included the development of an efficient method for the preparation of organotin fluorides, using anhydrous ammonium fluoride as the fluorinating agent. This technique was similar to that used in the preparation of fluorine-containing organophosphorus and organosilicon compounds (Appendices 3b and 4b). The method of preparation of tributyltin fluoride was:

$$(C_4H_9)_3SnOSn(C_4H_9)_3 + NH_4F \rightarrow (C_4H_9)_3SnF \leftarrow NH_4F + (C_4H_9)_3SnCl$$

Experimental details of the synthesis are given at Appendix 9a (Section 3.2.6, p. 13). This compound was one of the first new organotin compounds prepared by the author. Laboratory records show that the preparation(and toxicological assessment of tributyltin fluoride and other organotin compounds) was undertaken at MRL in August, 1958(Appendix 7). These initial activities formed the basis of an extensive future research effort on organotin fluorides (Section 5.7).

Using techniques similar to those used for the preparation of tributyltin fluoride, dibutyltin difluoride was prepared in good yields by the reaction of ammonium fluoride with dibutyltin dichloride, and triphenyltin fluoride by the reaction of the same fluorinating agent with triphenyltin chloride, oxide or hydroxide.

Although many mono-alkyl and mono-arylorganotin trichlorides, bromides and iodides have been reported (47, Table 12), our attempts to prepare a pure trifluoride compound were unsuccessful. Ammonium fluoride reacts vigorously with butyl and phenyltin trichlorides, but the crude wax-like products could not be purified.

Ingham, Rosenberg and Gilman (47, Table 20), van der Kerk and coworkers (74, 75) and Abel, Brady and Lerwill (76) reported new nitrogen-containing organotin compounds. We prepared new compounds of this type such as, tributyltin phthalimide, tributyltin succinimide and tributyltin isothiocyanate.

Tributyltin isothiocyanate was prepared by the reaction of potassium, silver or ammonium thiocyanate on tributyltin chloride, or on a mixture of bis(tributyltin) oxide and dilute hydrochloric acid:

$$(C_4H_9)_3SnCl + MSCN \longrightarrow (C_4H_9)_3SnNCS + MCl$$

where M = Ag, K or NH_4.

Tributyltin isothiocyanate was also formed from tributyltin cyanide (44) by reaction of sulphur dissolved in carbon disulphide. Bis (tributyltin) oxide was also reacted with thiourea to give tributyltin isothiocyanate and bis(tributyltin) sulphide, ammonia and water also being formed. The main product from this reaction was bis(tributyltin) sulphide, formed by an interchange between oxygen and sulphur.

$$(Bu_3Sn)_2O + H_2NCSNH_2 \longrightarrow Bu_3SnNCS + H_2O + NH_3 + Bu_3SnSSnBu_3$$

Substituted thioureas such as diphenyl, diethyl and dibutyl thiourea were also reacted with bis(tributyltin) oxide to give goods yields of bis(tributyltin) sulphide. Many of the nitrogen-containing organotin compounds prepared in the synthetic programme were used for detailed spectroscopic studies on the structure of organotin compounds (Section 5.6.3).

Details of the methods we used for the determination of tin, chloride, fluoride, nitrogen and sulphur in organotin compounds, are given at Appendix 9a (Section 3). The determination of fluoride was based on methods used previously by the author for the analysis of fluorine-containing organometallic compounds based on phosphorus and silicon (Appendices 3b and 4b).

Since this synthetic programme was undertaken, many new organotin compounds have been reported. The authoritative books by Stone and West (48), Dub (49), Poller (50), Sawyer (51), Abel and Stone (52) and Zuchermann (54) should be consulted for compounds of particular interest.

5.6 Infrared Studies on Organotin Compounds

5.6.1 Reporting of Spectra

In recent years, much has been written on the determination of the structure of organotin compounds by the use of infrared spectroscopic techniques. Poller (50) includes a chapter on the subject, and Sawyer (51) in his three volumes, refers extensively to infrared studies.

Gielen and others (77) have described special spectroscopic studies on the stereochemistry of complexes of Group IV metals, including tin.

In the early 1960's infrared studies on organotin compounds were not well developed. As our synthetic programme progressed, use was made of infrared spectroscopic techniques as a means for the identification of specific products from different reactions. Our surveys had shown that although over 800 organotins were known at that time, only about 100 compounds had been studied by infrared techniques and of these, only tetramethyltin had been studied in detail.

Because of the availability of reported and new organotin compounds at MRL, a detailed compilation and study of their infrared spectra was undertaken by the author in collaboration with R.A. CUMMINS. The infrared spectra of 198 organotin compounds, of which 41 were commercial products, were recorded over the frequency range 4000-450 cm^{-1}. About half the compounds examined were new materials. In addition, the infrared spectra of organotin compounds were reviewed and a bibliography of organotin compounds on which some infrared data had been published, was prepared.

In 1963, a comprehensive MRL report on the infrared spectra of organotin compounds was issued (78) and widely distributed. Requests for reprints were such that a second printing was necessary. As the report is now almost out-of-print the text is reproduced at Appendix 10a. Typical sample spectra are included for some organotin saturated carboxylates (Appendix 10a, Section 6.1, Spectra No. 1-12) and some organotin fluorides (Appendix 10a, Section 6.10, Spectra No. 1-6). We believe the report, which contained details of assignments of infrared vibrations involving tin-methyl groups and tin-X groups and extensive references, made a significant contribution to the advancement of infrared studies on organotin compounds.

Because of the availability of a library of spectra on organotin compounds, detailed structural studies were undertaken on organotin carboxylates (Appendices 10c and 10d) and on nitrogen-containing organotin compounds (Appendices 10e and 10f).

At the request of Sadtler Research Laboratories Inc., Philadelphia, USA, samples of new organotin compounds that had been synthesized at MRL (73, 78) were supplied and used by Sadtler for the compilation of a set of standard infrared spectra on organotin compounds. The spectra were issued in 1966 for commercial sale as part of a listing of 400 spectra designated, Organometallic Grating Spectra (79). The fifty-one spectra originating from MRL-supplied compounds were those in the series numbered

N186K, (Formyloxy) tributyltin to N237K, (Nicotinoyloxy) tributyltin. Examples are given at Appendix 10b, namely:

N229K Fluorotributyltin (Tributyltin fluoride)
N330K Fluorotriphenyltin (Triphenyltin fluoride)
N231K (Isothiocyanato)tributyltin (Tributyltin isothiocyanate)
N232K Succinimidotributyltin (Tributyltin succinimide)

With the Sadtler reported spectra, the frequency range over which recordings were made was 4000-250 cm^{-1}. The commercial availability of the Sadtler spectra stimulated further infrared studies on organotin compounds.

5.6.2 Organotin Carboxylates

At about the same time as the author was synthesizing new organotin compounds, several workers were studying the structure of methyltin carboxylates using infrared techniques. Okawara, Webster and Rochow (80) examined trimethyltin carboxylates and halides over the frequency range 3500-500 cm^{-1} and compared the carboxylate spectra with those of the methyl silicon carboxylates. Freeman (81) showed that dibutyltin diacetate had carboxyl absorption near 1588 cm^{-1} which was typical of acetate salts. Also Okawara and Sato (82) assigned bands in trimethyltin formate, acetate and monochloroacetate to the asymmetric and symmetric vibration of the carboxylate ion.

An alternative interpretation of the spectra of organotin carboxylates by Beattie and Gilson (83), proposed that the compounds could exist as chelates involving a 5-coordinated tin atom. Luijten, Janssen and van der Kerk (75) suggested an associated structure for certain carboxylates when in solution or as a liquid melt. Poller (84) also studied the carboxyl stretching frequency of organotin carboxylates, but was unable to distinguish between an ionic and a covalent structure.

Further studies by Janssen and coworkers (85) suggested that the structure of trialkyltin acylates, in the solid state, involved coordinated polymers with each tin atom 5-coordinated by three alkyl groups. In order to study the problem, a homologous series of tributyltin carboxylates ranging from the formate to the stearate and three substituted tributyltin acetates were prepared. Examination of the infrared spectra of the compounds confirmed the view that organotin carboxylates were covalent and chelated in character rather than ionic. This work, undertaken with R.A. CUMMINS, is reported at Appendix 10c (86). An interesting feature was the preparation of monobutyl (tributyltin) phthalate in order to study its infrared spectrum. With this compound, the normal C=O stretching

frequency near 1730 cm^{-1} due to the - $COOC_4H_9$ group was observed, while the C=O stretching frequency due to the - $COOSn(C_4H_9)_3$ group was shifted to near 1650 cm^{-1} (Appendix 10c, p.189).

Studies were also undertaken of the effects, on structure, of melting of solid organotin carboxylates and of temperature on the band intensities of tributyltin laurate. The results indicated that, in the solid state, organotin carboxylates existed as chelate compounds and this structure persisted in carboxylates that were liquid at room temperature. The chelate structure was broken down to the ester form by heat, or by solution. Since this work was undertaken many other authors have reported similar observations on organotin carboxylates (51).

As part of our studies on the fungicidal properties of organotin compounds (Section 5.9), the concept was developed of the synthesis of particular compounds that could contain, in the same molecule, trialkyl or triaryl groups to promote fungicidal activity and an ultraviolet light absorbing group to provide resistance to environmental degradation. Several organotin esters of 2-cyano-3,3-diphenylacrylic acid were prepared, their subsequent decarboxylation on heating examined, and studies undertaken on their structure. This conjoint study, undertaken with R.A. CUMMINS and D. OLDFIELD, is reported at Appendix 10d (87). The paper includes details of the synthesis of a number of triaryl and trialkyltin 2-cyano-3,3-diphenyl acrylates and their decarboxylation to the corresponding (1-cyano-2,2-diphenylethylene) triaryl and trialkyltin compounds. Thin layer chromatographic techniques were used to identify different products from the reactions, and infrared spectroscopic techniques to study the structure of various compounds.

With the trimethyltin ester, infrared studies on samples subjected to thermal treatment showed that an original monomeric ester form could be converted into one containing a pentacoordinated tin atom. We believe this was the first reported observation of polymorphism in organotin esters. None of the other esters of 2-cyano-3,3-diphenyl acrylate examined showed such changes and it was apparently only the trimethyltin ester that could exist in the chelate form.

Infrared studies were also undertaken on the CN stretching frequency and measurements made, in methanol, of the ultraviolet absorption characteristics of the esters. The latter study confirmed that retention of ultraviolet light absorption properties of the acrylate group had been achieved. In addition, this property was largely independent of the presence of the organotin group in the molecule or the absence of

the carboxyl group. Fungicidal activity was also retained in the trialkyl and triaryl organotin esters (Appendix 10d, p.2263).

Using compounds prepared at MRL, Cummins (88) independently investigated isomerism and inductive effects in tributyltin chloroacetates. Similar compounds were also reported, in 1971, by Yamaji and coworkers (89), who investigated the thermal decomposition of alkyltin halocarboxylates and the reaction between alkyltin oxides and carboxylic esters containing a halogen atom.

The tributyltin esters of mono-, di- and trichloroacetic acid were used as model compounds by Bocksteiner, Glew and Phillip (90), of MRL, as part of their studies on underwater marine coatings. Elimination reactions of tributyltin w-chloroalkanoates were further investigated as these compounds and their spectra had previously been studied, at MRL, as part of our work on organotin compounds (73,78,79).

5.6.3 Nitrogen-containing Organotins

As part of the synthetic programme of work on organotins, some new nitrogen-containing compounds were prepared (Appendix 9a, Section 2.7). Two of the more interesting compounds were tributyltin isothiocyanate and isocyanide. Following the preparation of these (and also tributyltin succinimide), infrared evidence was used to assign structures and to define reaction routes. Molecular refraction data were also used to support the structural assignments. This work, undertaken in conjunction with R.A. CUMMINS, is reported at Appendix 10e (91).

Although this work was reported in 1964, Poller (50, p.62) indicated that Stamm (92), on behalf of Stauffer Chemical Company, was issued a German patent, in 1965, for the preparation of tributyltin isothiocyanate using a method similar to that developed by the present author. The patent also suggested that the compound could be used as a catalyst for the preparation of polyurethane foams and as a pest control agent. Poller (50, p.91) also described in detail, the chemistry of compounds containing tin-nitrogen bonds. The same subject was comprehensively reviewed by Luijten and others (93), in 1965, and by Jones and Lappert (94), in 1966.

The first organotin isothiocyanate was prepared by Cahours (95), in 1862. Seyferth and Rochow (96), Seyferth and Stone (97), Anderson (98), Anderson and Vasta (99) and Seyferth and Kahlen (100, 101) reported the preparation of compounds designated as alkyltin *iso*thiocyanates or *iso*cyanides. The *isothiocyanates* could have the structure, *normal* thiocyanate,-SCN, or *iso*thiocyanate,-NCS.

In our work, tributyltin *iso*thiocyanate was prepared by reactions involving potassium, ammonium or silver thiocyanate and bis(tributyltin) oxide or chloride. It was also prepared by the action of thiourea on bis(tributyltin) oxide or sulphur in carbon disulphide on tributyltin cyanide. The reaction sequences are given at Appendix 10e, (91, p. 412). Detailed structural studies involving infrared intensity and frequency data for the band assigned to the -NCS groups in organotin compounds, suggested that the likely structure was that for tributyltin *iso*thiocyanate, $(C_4H_9)_3SnNCS$, rather than thiocyanate. This observation was supported by the use of molecular refraction data (Appendix 10e, 91, p. 415).

Similar studies were also undertaken on tributyltin *iso*cyanide. Although infrared and molecular refraction data on this compound were inconclusive (Appendix 10e, 91, P. 416), chemical evidence suggested that the compound existed mainly in the form of the isocyanide.

At MRL, using the method reported by Cummins and Dunn (91), a sample of tributyltin isothiocyanate was prepared with the abundance of the nitrogen-15 isotope enriched to 96%. Jenks (102) measured the spin-spin coupling constant between nitrogen-15 and tin-119 nuclei and its value was compared with other results, assuming that the Fermi contact term was the principal source of interaction. The application of ^{119m}Sn Mössbauer spectroscopy to the study of organotin compounds has been reviewed by Zucherman (103) in the series edited by Stone and West (48).

Recently an application of tributyltin isothiocyanate was reported by Plum and Runggas (104). Incorporation of 0.2-0.5 percent by weight, of Bu_3SnSCN into bituminous sealing materials, prevented penetration by roots of *Lupinus albus*. The sealants were suggested for use in the isolation of cables, pipes and conduits.

In 1970, Tsai, Lehn and Marshall (105) and Wiberg and Joo (106) reported on some interesting addition reactions being undertaken with trialkyltin azides. Working with D. OLDFIELD (107), a study was undertaken with tributyltin azide which had been prepared using reported procedures (75). Details of the work are given at Appendix 10f.

Tributyltin azide reacts with phenyl isothiocyanate to form 1-phenyl-4-(tributylstannyl) tetrazole-5-thione, which in turn can be broken down into 1-phenyltetrazole-5-thiol and tributyltin chloride. Similar addition reactions occur between triphenyltin azide and phenyl isothiocyanate. The reaction sequences are given at Appendix 10f (p. 646).

Reaction of tributyltin azide with carbon disulphide gives the cyclic thiatriazoline thione which is unstable and readily decomposes to tributyltin isothiocyanate, nitrogen and sulphur. In this study, infrared and ultraviolet spectroscopic data generated previously at MRL (91), was used to monitor the course of various reactions. Some of this work was discussed by Abel and Stone (52, p.154) in their review of the 1971 literature on organometallic chemistry. Detailed studies on the formation of organotin-nitrogen bonds by the 1,3-dipolar cycloaddition of trialkyltin azides to nitriles were also published, in 1971, by Sisido, Nabika and Isida (108).

Infrared studies on organotin compounds were also undertaken independently, at MRL, by Cummins, on isomerism in alkyltin compounds (109) and on the analysis of the band envelopes of the trans and gauche tin-carbon stretching frequencies (110). In conjunction with Evans (111) studies were also reported on the infrared spectra of some alkyltin oxides.

5.7 Organotin Fluorides

As described in Section 5.5, tributyltin fluoride (together with other organotin fluorides) was first synthesized at MRL, in 1958, using anhydrous ammonium fluoride as the fluorinating agent. Because of a special interest by the author in organometallic fluorides, a review of the history and applications of tributyltin fluoride has been undertaken.

The first report of tributyltin fluoride (and triphenyltin fluoride) was that of Russell (112), of MRL, who developed a colorimetric method for the determination of small amounts of tin using optical density measurements on a green reduction compound of silicomolybdic acid. The method was used for the analysis of bis(tributyltin) oxide in textiles. Russell assessed the purity of the new compounds, tributyltin fluoride and triphenyltin fluoride, which were supplied by the present author. The paper, published in December 1959, listed analytical results for both compounds, namely (112, p.715):

COMPARISON OF RESULTS BY COLORIMETRIC AND GRAVIMETRIC METHODS

Compound	Theoretical tin content %	Tin found by proposed method %	Tin found by gravimetric method %
Tri n-butyltin fluoride	38.35	37.00	37.40
Triphenyltin fluoride	32.16	31.30	31.35

In 1960, Mel'nikov (113) and others reported that tributyltin fluoride could be used for the protection of non-metallic surfaces against the action of microorganisms in place of organic mercury compounds. Similar work was reported a year later on the use of the same compound with mercury-free seed dressings (114).

The first report on the use of tributyltin fluoride as an antifouling agent appeared in 1963. Kageyama and Miyamura (115) evaluated an oleoresinous varnish containing 20 parts of tributyltin fluoride per hundred of formulated paint. In 1963, Dunn and Cummins (78) reported the infrared spectra of tributyltin fluoride and, in 1964, Dunn and Norris (73) described the synthesis of the same compound along with many other organotin compounds. A method for the preparation of tributyltin fluoride based on the reaction of potassium fluoride with tributyltin chloride was reported by Katsumura (116), in 1962.

The preparation of tributyltin fluoride and its purification by recrystallization from tetrahydrofuran was reported by Maruo and Furutaka (117). In 1968, Malnar (118) reported the synthesis of new trialkylfluorostannanes including tributyltin fluoride by the reaction of dibutyl mercury and stannous fluoride. The melting point was reported to be 341-2°C. In our work (73), the melting point of material recrystallized from methanol was found to be 218-19°C. Lorberth (119) reported the preparation of tributyltin fluoride from the corresponding chloride and potassium hydrogen difluoride in aqueous ethanol and, in 1970, we (Dunn and Oldfield, 120) described the preparation of the compound using tetrafluorohydroquinone as the fluorinating agent. In the same year, we (121) also reported on the properties of tributyltin fluoride as a novel coordination polymer in solution. Further studies on the preparation of tributyltin fluoride were reported, in 1974, by Ashley and Nackashi (122) and, in 1975, by Armitage and Tarassoli (123).

Studies on the infrared spectra of organotin fluorides, including tributyltin fluoride, in particular their covalent character, were reported, in 1965, by Brown and coworkers (124). Herber (125) used Mössbauer spectroscopy to study lattice dynamics and structure of tributyltin fluoride. Licht and others (126, 127, 128) in a series of papers used infrared and other spectroscopic data to show that tributyltin fluoride had pentacoordinate tin and strong intermolecular associations in the solid phase, and was monomeric in the vapour phase.

In studies on the correlation between chemical structure and fungicidal activity, Czerwinska and others (129) showed that tributyltin fluoride possessed very high activity. Associated authors (130) also

investigated the use of the same compound as a fungicide for plasticised poly(vinyl chloride) and, in 1970, Cardarelli and Neff (131) reported on its use as a means of producing fungal-and fouling-resistant elastomeric sheet materials. Japanese workers (132) reported on the use of tributyltin fluoride in organic solvents as fungicidal pastes and, earlier, Iwamoto and Kikuchi (133) described the very strong fungicidal activity of tributyltin fluoride against a number of test organisms.

Other reported applications of tributyltin fluoride included its use in antibacterial compounds (134), in rodent repellents in polyethylene cable sheathing (135), as a catalyst for alkylene oxide polymerization (136) and butadiene polymerization (137), as a chemosterilant against the females of the housefly species *Musca domestica* (138), as a control for blackfly (139), as a herbicide for the control of weeds in corn, rice, pea and peanut crops (140) and as a fungicide in abrasion-resistant strings made from polypropylene (141). The toxicological properties of tributyltin fluoride were reported by Nakayama and coworkers (142).

During the last decade the major use of tributyltin fluoride has been in antifouling paints and related compositions. In 1968, Perkins, Milne and Hearson (143) described the use of an antifouling marine paint based on a film-forming matrix containing 50% by weight, of synthetic polymer and 20-75% by volume, of tributyltin fluoride. Morgan (144) Murayama and others (145), Freeman (146), Skinner (147, 148) and De Nio (149), during the period 1970-74, all reported on the use of tributyltin fluoride in paint-type compositions suitable for use on the hulls of ships.

The antifouling performance of tributyltin fluoride in epoxy-based compositions was reported by Beers (150), Neffgen and Plum (151) and Plum (152), in epoxy or polyester, glass-fibre reinforced laminates by Plum and Von Haaren (153), and in chlorinated rubber-based coatings by Rascio and coworkers (154) and, at MRL, by Pettis, Phillip, Smith and Wake (155). Its use in natural and synthetic rubber was described by Conger and Evans (156) and Kitani, Ohhata and Ninomiya (157).

In 1975, Sheldon (158) described the effects of organotin antifouling coatings on man and his environment and reported that in rats the acute oral LD50 value of tributyltin fluoride was 200 mg/kg. Dermal toxicity studies on rabbits were also undertaken. For comparison, the author, in 1958, reported that the probable MLD 100 value for tributyltin fluoride was 30 mg/kg (Appendix 7a). Results of comparative testing of biological activity of organotin (including tributyltin fluoride) and organoarsenic compounds used in antifouling paints were reported in 1976 by Izral'yants, Kudinova and Basova (159).

This brief review indicates the progress that has been made in the study of tributyltin fluoride (and other organotin fluorides) during the last two decades. Work undertaken at MRL forms part of these world-wide activities. The author (and colleagues) initiated several programmes at MRL, the aims of which were to assess organotin compounds, particularly tributyltin fluoride and polymeric organotins in potential military applications. These investigations are reported in Section 5.9. During the same period, fundamental investigations were carried out using tributyltin fluoride.

During studies on the synthesis of tributyltin fluoride (73) and efforts to purify the compound for analysis, unusual properties with different solvents were observed. Although insoluble in many solvents, tributyltin fluoride could be recrystallized from methanol to give fine, white, needle-like crystals with a well-defined melting point. With some solvents it formed very viscous solutions. In conjunction with D. OLDFIELD, a study was undertaken on the properties of the solutions formed with non-polar organic solvents and on the effects of certain compounds that, when added to the solutions, caused marked changes in viscosity. Details are given at Appendix 11a (121).

In 1968, Davies (160) reviewed the formation of penta-coordinate complexes of organotin compounds when bound to suitable ligands. Janssen and others (161) showed that tributyltin imidazole existed as linear polymeric chains in solution in toluene, as well as in the crystalline state. In our work, we showed that tributyltin fluoride could be dissolved to the extent of about 2% by weight, in methanol to give non-viscous solutions, and to the same extent in carbon tetrachloride or n-hexane to give very viscous solutions. In these viscous solutions, it was postulated that the penta-cordinate tin atoms were present with fluorine acting as the bridging atom to form a polymer (Appendix 11a, p.1162). As the interaction of organotin fluoride molecules in solution was only electrostatic in nature, the polymer could be easily disrupted by the addition of certain compounds.

Additives such as toluene, chloroform, methanol and various amides and amines caused a marked reduction in the viscosity of the viscous solutions by breaking down the polymeric tributyltin fluoride to a type of complexed monomer. In these cases, the organotin compound comprised a penta-coordinated tin atom bonded to a molecule of the additive, three n-butyl groups, and a fluorine atom. Spectroscopic studies on the forms in which tributyltin fluoride could exist, have also been reported by Licht and coworkers (126, 127, 128).

In our early work (73), tributyltin fluoride was prepared by the action of ammonium fluoride on bis(tributyltin) oxide. The technique was then refined by dissolving the oxide in toluene and adding an aqueous solution of ammonium fluoride while stirring vigorously at room temperature. This method was similar to the interfacial condensation procedure for the preparation of organotin esters reported by Frankel and others (162). During studies involving fluorinated phenols, tributyltin chloride was reacted with tetrafluorohydroquinone and instead of the expected compound, tributyltin fluoride was formed. The same compound was also formed by the reaction of bis(tributyltin) oxide and tetrafluorohydroquinone. Details of this work are given at Appendix 11b (120). The coauthor in this work, D. OLDFIELD, working independently also developed a method for the preparation, by the interfacial technique, of tributyltin pentafluorophenate by reaction of pentafluorophenol with tributyltin chloride (163).

In studies on the preparation of fluoroaromatic-substituted organotin compounds, we investigated γ-irradiation induced reactions between organotin compounds and pentafluorobenzene. A typical reaction resulted in the production of a copious precipitate of tributyltin fluoride from the γ-irradiation of tetrabutyltin in pentafluorobenzene. Similarly, irradiation of hexabutylditin in pentafluorobenzene yielded small amounts of dibutyltin oxide from trace impurities such as water, or oxygen and dibutyltin difluoride. Details of this work, which was undertaken with D. OLDFIELD, are given at Appendix 11c (164).

5.8 Miscellaneous Organotin Activities at MRL

At MRL, some studies were undertaken by others on organotin compounds, and several of these are described in Section 5.9.

D. Oldfield, as well as collaborating with the author in some of the programmes already described, initiated and conducted some further research on organotin polymers. In 1975, he reported (165) on the interfacial preparation and properties of poly(tributyltin acrylate) and related polymers. This work was extended (166) to the synthesis of organotin polymers with molecular weights of around 500,000. Acrylic acid was first polymerised in aqueous solution and then neutralized with sodium hydroxide. Interfacial condensation reaction between this solution and an organotin chloride in dichloromethane produced the organotin polymer in the organic phase. This method is potentially very versatile for producing polymers containing a range of organotin groups with higher purity and molecular weights than can be achieved using conventional peroxide polymerisation. An interferometric study of some of these

organotin polymers was undertaken, at MRL, by C.E.M. Morris (167).

5.9 Applications of Organotin Compounds

5.9.1 General

In recent years, there has been an awareness of the need to fully utilize the results of basic and applied research, by extending studies to the stage where product development is possible. In Australia, this matter has been of some concern especially in relation to government funded research and development activities and the future of local manufacturing industry. Recent inquiries have studied the problems in some detail (168, 169, 170).

At MRL, our work (as indicated by the Annual Report, 166) is directed to establishing and maintaining scientific and technical expertise in particular fields relevant to the supply and operation of defence materiel. As part of these activities, investigations have been undertaken on applications of organotin compounds as additives to improve the long-term performance of organic materials. Two areas have attracted particular attention namely, marine applications and antifungal applications.

5.9.2 Organotins in Marine Applications

Poller (50, p.281) has summarized some earlier work on antifouling activities on organotin compounds, and more recently Phillip (171) has discussed modern trends in marine antifouling paint research, including the use of organotin compounds. Oldfield (172) has also discussed the use of organotins in polymer chemistry.

At MRL, several workers investigated organotins as toxicants for use in marine paints for naval applications. Phillip, Bocksteiner, Pettis and Glew (173) developed some trialkyltin polymers and copolymers as vehicles for use in antifouling paint. De Forest and others (174) investigated elastomeric antifouling coatings containing organotin toxicants and undertook marine exposures in tropical waters in Northern Australia. The evaluation of organotin antifouling paint (containing tributyltin fluoride) for use on glass reinforced plastics hulls, was reported by Pettis and Wake (175). In 1976, much of the work undertaken at MRL on coatings containing organotin compounds was summarized in a report by Bocksteiner, Phillip and Wake (176). Further work on antifouling coatings based on organometallic polymers and organic biocides was undertaken, at MRL, by Jackson (177).

While much of this work was in progress, the author proposed that natural and synthetic rubber sheet materials containing organotin toxicants

warranted investigation as antifouling materials. Using data acquired in the early 1960's during investigations on organotins in natural and synthetic rubbers for use in antifungal applications (65, Appendix 8, p.8.2), formulations were proposed for investigation. This work was then undertaken by Woodford (178), who incorporated up to 7.6% by weight, of organotin compounds, such as tributyltin fluoride and acetate and bis(tributyltin) oxide, into several elastomers in order to investigate their antifouling activity. The elastomers used by Woodford were polychloroprene, nitrile and natural rubber, formulated with conventional sulphur-based curing agents, antioxidants and carbon black. Immersion trials on these vulcanizates undertaken over a period of two years on a test raft in Sydney Harbour, indicated that substantial antifouling activity could be achieved.

Certain organotin compounds however, seriously retarded the cure of the elastomers and about 10% by weight, of some toxicants was usually the maximum that could be incorporated if acceptable mechanical properties were to be retained. As part of this work Wake (179), using vulcanizates from the trial arranged by Woodford (178), reported on the antifouling activity of three organotin compounds incorporated into nitrile rubbers.

In late 1970, the author proposed a new concept in antifouling rubbers in order to overcome the problems observed by Woodford (178). Work was then undertaken with D. OLDFIELD on the development of a new system of antifouling rubbers using organotin compounds as the primary toxicants. A copy of the original proposal is given at Appendix 12a.

In order to increase the amount of toxicant present in a vulcanizate while retaining good mechanical properties, an unsaturated organotin monomer, such as tributyltin acrylate, was added to the rubber formulation and the whole system then crosslinked, or cured, by use of a suitable peroxide. With this new system three reactions were possible namely, crosslinking of the elastomer (vulcanization), homopolymerization of the organotin monomer or, finally, covulcanization of the elastomer and the organotin compound. With high levels of organotin toxicants, the mechanical properties of the peroxide-cured system were superior to those of the sulphur-cured system as the cure was not retarded.

In this study, eleven different types of elastomers and one plastics were examined. In order to promote quick release of toxicants into seawater, some monomers such as bis(tributyltin) oxide, tributyltin acetate and tributyltin fluoride were used as additional components in certain covulcanized systems. The usual level of tributyltin acrylate present was 15% by weight, but for experimental purposes vulcanizates with

total organotin contents ranging from 7.5% by weight, to 50% by weight, were used. Details of the mechanism of covulcanization, types of formulations used and mechanical properties are given at Appendix 12b (180).

Following laboratory evaluation of the vulcanizates, a marine immersion trial over a period of two years was undertaken at tropical and temperate sites in Australia. Results showed that tributyltin acrylate could be incorporated into elastomers and then cured with peroxides to give vulcanizates with excellent mechanical properties. These properties were substantially retained after long periods of marine immersion, and the vulcanizates were highly effective in the prevention of growth of marine fouling on their surfaces. Those of particular interest were chlorosulphonated polyethylene, ethylene-propylene terpolymer, natural rubber, styrene - butadiene, polybutadiene, nitrile-poly(vinyl chloride), polychloroprene and nitrile rubber. Although carbon black reinforced vulcanizates were preferred, satisfactory properties were obtained when either calcium carbonate or clay was used as a non-black filler. The most promising systems investigated would be expected to have superior performance to that previously reported for conventional antifouling rubbers.

The original public disclosure of this work was made at the Third Australian Rubber Technology Convention, organised by the Institution of the Rubber Industry, Australasian Section, Terrigal, New South Wales in September, 1974. The work attracted the favourable critical approval of Prof. N. Cardarelli, Associate Professor, General Technology, University of Akron, USA (181) who has pioneered most of the recently reported work on biologically active rubbers and plastics (182).

5.9.3 Organotins in the Protection of Timber

The Royal Australian Navy has had in service for many years, a number of wooden-hulled minesweepers. The timber used in the construction of the hull was West African mahogany, *Khaya ivorensis*. A number of highly specialised, wood-boring bivalve molluscs (*Teredinidae*), generally known as shipworms or borers, voraciously attack timber under suitable conditions, and destroy its structure and strength by boring tunnels through it. To prevent this attack it was necessary to apply a sheathing, resistant to attack by shipworms, to the hull.

During construction, the minesweepers were sheathed using the *Cascover* process (183), which consisted of a heavy-duty, nylon fabric bonded to the hull with a resorcinol-formaldehyde adhesive. A poly(vinyl chloride) coating was applied to the fabric and this was then treated

with antifouling and camouflage coatings. Although the sheathing was effective in preventing penetration of the hull by shipworms, difficulties were experienced, in tropical and temperate waters, because of blistering of the sheathing, failure of the adhesive and mechanical damage.

Alternative sheathings were sought by Navy for application to the hulls, during refits. Preliminary trials indicated that glass-reinforced, epoxy resins could be bonded to a wooden hull, following removal of the *Cascover* sheathing and subsequent cleaning. Because glass-reinforced resins were known to have good resistance to penetration by shipworms, these materials were selected for reconditioning the hulls.

In this programme, the opportunity was taken to investigate the use of organotin compounds as impregnants for timber in order to prevent attack by shipworms. This work, which was undertaken in conjunction with G.F. SANSOM, has been described in an MRL report (184). The cover and contents pages and list of tables and figures are given at Appendix 12c.

The use of *Khaya ivorensis* for the hulls of non-magnetic naval vessels is common practice and a comprehensive manual on the use of wood in naval ships, is available (185). Metcalfe and Chalk (186) have described the structure of *Khaya ivorensis* in detail and some typical scanning electron micrographs of longitudinal and transverse sections are shown at Appendix 12d. These micrographs were produced by S.R. Silva and V.M. Silva, both of MRL, using the techniques described by Scurfield and Silva (187, 188).

Shipworms can rapidly infest panels of *Khaya ivorensis* to cause the damage shown at Appendix 12e. This damage was revealed by use of a non-destructive radiological examination of panels. We are indebted to W. Hemmy, MRL, for performing these examinations. X-rays from a beryllium-windowed tube, at a distance of 1.5m to minimize geometric distortion, and an operating voltage of 22-30 kv, were used. A radiograph of an epoxy resin, fibreglass-reinforced, coated panel showing penetration by shipworms, is given at Appendix 27a, Figure 4.

Treatment of the timber by selected toxicants can retard or prevent this infestation by shipworms. In addition to the use of well known toxicants such as creosote (189), certain organotin (50) and organolead (190) compounds are claimed to be effective in the protection of timbers. Panels impregnated with either bis(tributyltin) oxide or tributyltin fluoride were used in our immersion trials. The tributyltin fluoride toxicant was formed within the timber panel by the reaction of

bis(tributyltin) oxide and ammonium fluoride.

Impregnation with bis(tributyltin) oxide was carried out by immersion of preconditioned panels in a solution of the toxicant in acetone for a period of seventy-two hours. After immersion, the panels were air dried and the drying was completed by heating in an air oven at 50°C for six hours.

Impregnation of timber with tributyltin fluoride was carried out by initially impregnating with bis(tributyltin) oxide. The panel was then immersed in an aqueous solution of ammonium fluoride for seventy-two hours. After immersion, the panel was air dried for twenty-four hours and finally dried at 50°C. Reaction of the ammonium fluoride and bis(tributyltin) oxide to form tributyltin fluoride *in situ*, was completed by further heating the panel at 120°C for one hour. In this manner crystalline tributyltin fluoride was formed within the structure of the timber, as shown at Appendix 12d. We believe this method of impregnation of timber with an organotin compound, by reaction *in situ* within its structure, is unique.

In selecting underwater coatings for timber, care was taken to ensure that the systems chosen were suitable for application under conditions normally encountered in naval dockyards. The systems selected included: polyester resin, unreinforced and glass-reinforced epoxy resin, silica-reinforced polychloroprene rubber, carbon black-reinforced polychloroprene rubber, resorcinol-formaldehyde resin, chlorosulphonated polyethylene rubber, poly(vinyl chloride) resin, acrylic emulsion and chlorinated rubber.

Over a period of some years, several major trials were undertaken. All specimens were prepared at Defence Standards Laboratories, Maribyrnong, Victoria, and trials were undertaken at the Joint Tropical Research Unit, Innisfail, North Queensland. As well as coated timbers, some uncoated timbers impregnated with organotin toxicants were also evaluated. From these trials, four coatings were found to have an excellent performance in the marine environment namely, an epoxy resin, a chlorosulphonated polyethylene rubber, a silica-reinforced polychloroprene rubber and a poly(vinyl chloride) resin.

Organotin toxicants, especially bis(tributyltin) oxide and tributyltin fluoride, were also shown to be effective impregnants for use with the timber *Khaya ivorensis*. They conferred increased resistance to attack by shipworms either alone, or as an additional protection to that afforded by the use of organic coatings.

Following this work, Oldfield and Sansom (191) investigated

the effectiveness of six organic coatings containing organotin toxicants as protective coatings for timber in order to prevent marine fouling. Tributyltin fluoride was one of the compounds investigated.

Since this work was undertaken there have been further reports on the use of organotins for the protection of timber. The use of bis(tributyltin) oxide and triphenyltin acetate, in solvent to impregnate wood to give protection from attack by fungi and insects, has been described recently by Schmitt and coworkers (192).

5.9.4 Organotins as Fungicides for Rubbers

As described in Section 5.4, work was undertaken by the author in the early 1960's on elastomeric and fungicidal organotin compounds, and a summary was presented in 1962 (65). This involved the protection of rubbers (and plastics) by the use of organotin compounds added to the rubber formulation prior to vulcanization. The approach was a traditional one to an ever present problem.

During the Vietnam war sensitive optical and electronic military equipment was rapidly rendered unserviceable by the growth of microorganisms such as fungi. The problem is still serious in tropical areas and usually results in the use of elaborate and costly sealing procedures. Upsher (193) has described some of the problems associated with microbial attack on materials.

A common method of sealing sophisticated military, industrial and commercial equipment is by the use of O-rings and similar types of seals. These are only of value, if they can be shown to effectively prevent the ingress of fungi. Fungicides are often incorporated into these rubbers but usually only have limited lifetimes due to their depletion by hydrolysis, leaching, blooming or evaporation from the rubber surface. In addition, many of the fungicides contain heavy metals such as copper and mercury and these often promote deterioration of substrate materials. Chlorine-containing fungicides are prone to cause corrosion of, and adhesion to, metallic components. Kerner-Gang (194) has described evaluation techniques for resistance of optical lenses to fungal attack and indicated the importance of maintaining optical clarity in fungal-free systems.

In the early 1970's, the author initiated a programme the aim of which was to develop a new system of antifungal rubbers and to evaluate their performance in conjunction with a number of substrates based on plastics, metals and glass (195). This work was undertaken in collaboration with D. OLDFIELD (Appendix 13a).

Using a modification of the system developed, at MRL by Dunn and Oldfield (180), to prevent the growth of marine fouling on underwater surfaces, we produced elastomeric vulcanizates suitable for use in sealing applications and which possessed long-term fungicidal properties. Thus conventional, monomeric fungicides were replaced by polymeric organotin compounds covulcanized into the rubber network. Polychloroprene, acrylonitrile-butadiene rubber and ethylene-propylene terpolymer are three rubbers commonly used in military equipment and these can all be covulcanized with tributyltin acrylate in the presence of peroxides, to give vulcanizates with a powerful and long-lasting fungicidal action.

To assess the long-term performance of these new fungicidal O-rings, special test assemblies were developed. Each assembly consisted of a circular aluminium base plate with three holes equidistantly spaced from the outer edge. Three stacks of ten discs of different materials each with a central hole were placed so that all of the holes were collinear. Between each pair of surfaces, one large control O-ring and one small fungicidal O-ring of the same rubber were placed concentrically to form an annular cavity sealed by the two rings. Two O-rings were placed similarly on the top of each stack, a top plate added and the assembly bolted together.

The ten metallic, glass and plastics materials used in the assemblies were: aluminium plate (a magnesium-aluminium alloy with good resistance to corrosion by seawater), commercial stainless steel, nylon 11, poly(methyl methacrylate), acrylonitrile-butadiene-styrene, polypropylene rigid poly(vinyl chloride), glass reinforced polyester resin, polycarbonate and plate glass.

The assemblies were assessed in laboratory and field trials over a three-year period. Sealed cavities formed between the O-rings and glass, seven different plastics, stainless steel and aluminium remained dry and free from microbiological growth during exposure to several adverse environments.

The long-term compression set of the O-rings was greater than predicted from conventional short-term tests at elevated temperature. Other mechanical properties were not greatly affected by the trial exposures under 15% compression. Certain combinations of elastomers and plastics would not be recommended for applications where ease of separation after long periods of compression was important. The elastomers did not

promote stress cracking in any of the plastics; optical properties of transparent materials were also unchanged. The incorporation of polymeric organotin fungicides into the rubbers effectively prevented fungal contamination of the O-rings and adjacent areas. The technique is suitable for use with most hydrocarbon rubbers.

Public disclosure of this work was made at the Fourth Australian Rubber Technology Convention, sponsored by the Plastics and Rubber Institute, Australasian Section, in Queensland, October 1977. At the Convention, the paper, which was issued as an MRL report (196), was awarded the inaugural Jim Smithson Medallion. The paper has recently been published in Britain (197), and a reprint is given at Appendix 13a.

As part of this programme a new, simple technique, based on the change of hardness of a nylon indicator disc, was used to determine the extent of ingress of moisture into sealed cavities. We believe this technique could have further applications in long-term environmental trials, under adverse conditions, where it is important to monitor changes in humidity and water content in sealed systems.

This work, together with our work on the use of organotins in antifouling applications, is based on the controlled release of toxicants from polymeric substrates. The recent book by Paul and Harris (198) summarizes the current state-of-the-art activities in the field of controlled release technology.

5.9.5 Organotins as Fungicides for Plasticised Poly(vinyl chloride)

Plastics materials are susceptible to attack by fungi, bacteria, insects and rodents as well as to ultraviolet radiation and other factors associated with weathering. The microbiological deterioration of rubbers and plastics has been discussed in a comprehensive review by Heap (199), and others (200), while Pacitti (201) has reviewed the attack of rubbers and plastics by other agents, such as insects and rodents. Recently, Pantke (202) described test methods for evaluation of susceptibility of plasticised poly(vinyl chloride) and its components to microbial attack, and Osman and Klausmeier (203) have described techniques for assessing biodeterioration of plastics and plasticisers. In collaboration with E.J. HILL, studies were initiated to assess the effectiveness of a number of fungicides incorporated into plasticised poly(vinyl chloride). Fungicides used in this study were either organotin compounds or commercial

organic fungicides of known composition. Trialkyl and triaryl organotin compounds have good antifungal properties, as reported by Luijten and van der Kerk (44) and Ingham and coworkers (47). Dialkyl and diaryl organotin compounds are not fungicidal but are widely used as stabilizers for plasticised poly(vinyl chloride) (204). Because of doubts concerning the ultraviolet light stability of the trialkyl and triaryl organotin compounds (205), trials were designed to assess this property under typical service conditions.

Thirty-six organotin compounds were assessed in the laboratory and of these nine compounds were selected for field trials. The compounds were: poly(tributyltin methacrylate), bis(tributyltin) sebacate, bis(tributyltin) oxide, tributyltin fluoride, triphenyltin fluoride, bis(tributyltin) terephthalate, tributyltin fumarate half ester, bis(tributyltin) maleate and poly(tributyltin acrylate).

Of the thirteen commercial fungicides assessed in the laboratory, nine were selected for field trials. The compounds were: pentachlorophenyl laurate, N-(trichloromethyl thio) phthalimide, N-trichloromethyl mercapto-4-cyclohexanone-1, 2-dicarboximide, 5,6-dichloro, 2(3H)-benzoxazolone, a derivative of parachlorometaxylenol, 3,4,7,8-tetramethyl-1, 10-phenanthroline and its hydrochloric acid salt and 2,9-dimethyl-1,10-phenanthroline and its hydrochloric acid salt. In an attempt to reduce the degradation of the organotin fungicides by ultraviolet light, certain ultraviolet absorbers were used in several selected compounds.

Field trials were conducted at tropical and temperature sites in Australia. The results of this work have been reported by Dunn and Hill (206), and the title and contents pages of the report are given at Appendix 14a. The report showed that the addition of organotin or organic fungicides to plasticised poly(vinyl chloride) compounds did not cause any reduction in original physical properties. Organotin fungicides were superior to most commercial organic fungicides in their resistance to thermal degradation during processing. Poly(vinyl chloride) compounds containing plasticisers susceptible to fungal attack continued to support fungal growth even in the presence of 0.2% by weight, of fungicide. Exposure of poly (vinyl chloride) compounds for 18 months under temperate, desert and tropical conditions was sufficient to destroy the activity of many fungicides. Organotin fungicides, however, when protected from degradation by ultraviolet light, retained some fungicidal activity.

Poly(vinyl chloride) compounds with good fungal resistance were obtained, without inclusion of fungicides, by the use of fungal-resistant

plasticisers such as dinonyl phthalate and tricresyl phosphate. These compounds showed good retention of physical properties. Improved resistance to weathering of these compounds by the addition of an organotin compound, such as tributyltin fluoride, and an ultraviolet absorber was considered to be a realistic possibility.

Compounds containing 0.5% by weight, of organotin additive together with an ultraviolet absorber were shown to exhibit improved resistance to weathering, even at sites with severe environmental exposure conditions. Other compounds containing dinonyl phthalate and tricresyl phosphate as plasticisers, also showed good retention of properties following prolonged outdoor exposure.

Evaluation of the effects of weathering on plasticised poly (vinyl chloride) compounds using conventional mechanical tests such as tear strength, tensile strength and hardness did not, in most cases, give an accurate indication of overall performance. Determination of elongation at break properties appeared to be a realistic method for assessing resistance to weathering. Studies on the polymer itself, however, were necessary in order to fully evaluate the effects of weathering. The cover and content page of the report on this work (207) are given at Appendix 14b.

In conjunction with D. OLDFIELD and R.H. STACEWICZ, loss of plasticiser during exposure, and some initial studies on polymer degradation, were undertaken. A reprint of the paper (208) is given at Appendix 14c. In this work, an empirical correlation was established between loss of plasticiser by evaporation during exposure, and the average daily maximum temperature at each site (Appendix 14c, p. 2109). The general effectiveness of organotin compounds and ultraviolet absorbers in the prevention of deterioration of poly(vinyl chloride), was estimated by measuring the viscosity of the polymer, in solution, after exposure. Results from this method of assessment were compared to those from traditional mechanical tests.

These results indicated further work was necessary on the use of organotin compounds and ultraviolet absorbers as additives for poly(vinyl chloride), plasticised with dinonyl phthalate or tricresyl phosphate. Studies were initiated which involved the development and investigation of thirty-two formulations containing additives to improve resistance to weathering. This work, which was undertaken in collaboration with D. OLDFIELD and G.F. SANSOM, was presented at an international symposium in London, in 1976 (209). The paper is given at Appendix 14d.

From the overall assessment of the compounds, five which were the most resistant to weathering all contained an organoarsenic-soya bean derivative as a secondary plasticiser and barium metaborate filler. The additives which gave improved resistance to weathering were: copper-8-hydroxyquinolinate; 2,4-thiazolyl benzimidazole; 2-hydroxy-4-methoxybenzophenone; and nickel dibutyldithiocarbamate in various combinations. Tributyltin fluoride was inferior to the above additives. A significant result of this work was the observation that copper-8-hydroxyquinolinate, which is normally considered to be a fungicide, also markedly improved the weathering characteristics of plasticised poly (vinyl chloride). Materials with the ability to withstand continuous outdoor exposure for five years under very severe Australian environmental conditions have been identified, developed and assessed. This work should result in the use of improved plasticised poly(vinyl chloride) materials in military, industrial and commercial applications.

5.10 Conclusions

Since the early 1950's, when the pioneering work of Luijten and van der Kerk (43) on the systematic study of the biological effects of organotin compounds was initiated, research into the chemistry and properties of these compounds has received considerable attention. Significant progress has been made on the synthesis of new organotin compounds, on studies of basic reactions and structures, and on the introduction of new and novel applications.

Organotin compounds are now considered as essential materials for use in the stabilization of many plastics, particularly poly(vinyl chloride), as catalysts for the production of foams and for use in cold-curing rubbers, and, because of their biological properties, as biocides, insecticides, rodenticides, mollusicides, bactericides and antifouling agents. Significant applications of organotins should continue to be found in the agricultural, industrial, medical and veterinary fields.

The applied research activities initiated and undertaken by the author and colleagues, at MRL, have contributed to studies on organotin compounds. It is expected that future work on the development of organotins as special additives for use with organic materials, will result in improved products with even greater versatility and durability than exists at present.

PART II. APPLIED RESEARCH ON ORGANIC MATERIALS

6. SCOPE OF ACTIVITIES

Since the late 1950's, the author has been responsible for undertaking applied research on organic materials of interest to the Defence Forces. Some of these activities are described in Part I (Section 5.9, in particular).

As part of this work, Service items found to be deficient in any respect were examined and attempts made to upgrade performance. Critical assessments of the organic materials components were made in order that improved materials could be introduced and the life of items extended. This stimulating and challenging applied research often resulted in unexpected problems being encountered. One such problem was the stress cracking of polyamides.

Other interesting problems concerned with elastomeric materials included: new seals for plastics components; the development of non-black, ethylene-propylene diene rubbers; new rubbers for combat footwear; rubbers with interesting electrostatic properties; the tropical deterioration of rubber; magnetic rubbers;and special rubbers for use in detonantless fuzes. Some plastics problems included: the development of coated fabrics for use in the tropics; the weathering of polyolefins; the recording of unusual imprints of barnacles on coating materials;and the fire hazards of organic materials.

7. STRESS CRACKING OF POLYAMIDES

7.1 Failure of Components

In the early 1960's, the Australian Army took delivery of an initial batch of prototype field telephones having nylon 6 cases and designated as *Telephone Set K*. The telephones were made in accordance with a provisional Army specification (210) and were available for laboratory and field evaluation. Later, formal specifications were issued to cover the telephone and components (211, 212). Details of the main case, handset and sealing rings, are shown at Appendix 15a.

After some time, severe cracking and delamination of the nylon 6 case adjacent to the battery compartment was noticed in two of the prototypes, and the damaged cases were submitted to Materials Research Laboratories for examination. An investigation into the cause of failure was undertaken in collaboration with A.J.C. HALL and T. NORRIS.

Two dry cells located in a compartment at one end of the moulding provided the power that allowed the set to function. Cracking of nylon 6 telephone cases occurred when electrolyte had leaked from discharged dry cells located in the battery compartment. Investigation of the cracking showed that aqueous zinc chloride solutions varying in concentration from 20% to 80% (w/v) were effective in producing the failures observed. Initial publication of our observations (213) was made in 1962 and the paper is reproduced at Appendix 15b. Included in the paper was a photograph (213, Fig 1) showing the stress cracking induced in nylon 6 by the use of 80% aqueous zinc chloride solution at room temperature. An enlargement of the original photograph is reproduced at Appendix 15c. Our observations (213) were consistent with those of Ensanian (214) who reported that concentrated hydrochloric acid alone, or a mixture of hydrochloric acid, alcohol and zinc dust would cause rapid failure of a stressed nylon strip.

Stressed specimens of nylon 6 when *immersed in* zinc chloride solution did not crack as severely as when discrete drops of solution were allowed to remain in contact with them. Mouldings treated with 80% zinc chloride at room temperature cracked in about 60 minutes, whereas a 50% solution required 120 minutes and a 30% solution, 300 minutes. Although the stress cracking of plastics by organic chemicals is not unusual, the observed action of aqueous zinc chloride on stressed nylon, was surprising. The phenomenon of the rapid failure of certain nylons by zinc chloride could be analogous to the cracking of metals by the action of liquid metals (215).

In conjunction with T. NORRIS, a detailed study was undertaken on the stress cracking of nylon mouldings by zinc chloride. The objectives of the study were to be able to provide Army with either a means for the prevention of stress cracking in nylon 6 mouldings or, alternatively, a choice of materials resistant to stress cracking from which mouldings could be produced using existing tooling. The cover page and contents pages of the report (216) issued on this study, are given at Appendix 15d.

When a single drop of 80% zinc chloride solution was applied to a stressed nylon 6 moulding, cracking extended to areas up to 150 mm from the drop. Chemical examination of cracked sections remote from the drop showed the presence of zinc chloride, and the indications were that the zinc chloride moved rapidly, by capillary action, along the cracks as they propagated. Investigation also showed that the type of nylon, temperature,

the water content of the nylon, concentration of zinc chloride solution, and the level of stress in the moulding,were all important factors.

In studies on the effect of temperature on stress cracking of nylon components by zinc chloride, rates of crack growth, at 50°C, of the order of 10 mm per minute were observed. The rate was critically dependent on the water content of the nylon. Mouldings containing less than approximately 1.5% by weight, of water did not crack in the presence of zinc chloride. Nylon 6 mouldings, annealed in hot oil for two hours at 160°C, remained in contact with 80% zinc chloride for nine months before cracks were observed and were thus relatively resistant to attack. When the water content of mouldings was increased beyond 1.5% however, either by water conditioning or by exposure to a humid atmosphere, cracking occurred following contact with 80% zinc chloride solution. As the equilibrium moisture content of nylon 6 usually exceeds 1.5%, it was thus unlikely that *any* treatment of nylon 6 mouldings would give long-term resistance to attack by zinc chloride.

Different types of nylons have specific water absorption characteristics, and the effect of zinc chloride on components moulded from nylon 6, 66, 610 and 11 was investigated. Measurements were made of the water uptake of these nylons when exposed in the jungle in tropical Australia. The relationship between water uptake and time of exposure is given at Appendix 27a, Figure 5.

Nylon 11, polyundecanoamide, was shown to be resistant to stress cracking by zinc chloride and was recommended as being suitable for general-purpose military use. It was available in both plasticised and unplasticised grades,and case mouldings were produced with dies originally designed to mould nylon 6. Mouldings were exposed,at 50°C,to conditions of high humidity and then tested for resistance to zinc chloride. Both plasticised and unplasticised grades were resistant to attack.

Following these investigations black, plasticised, nylon 11 was specified, by Army, for use in components for military telephones. Detailed basic studies were then initiated to investigate the mechanism of stress cracking of polyamides by metal salts (Section 7.2).

In 1978, the opportunity arose to assess the extent of moulded-in stress in some safety glass frames moulded from nylon 6. The component is shown at Appendix 15e (top). Drops of 80% zinc chloride were applied to

the frame at the points indicated at Appendix 15e (middle). The plastics injection points for the moulding are indicated by I_1 and I_2. The effect of zinc chloride is shown at Appendix 15e (bottom). Crack initiation was observed after 12 minutes and fracture after 45 minutes.

Following this evaluation, modifications to the moulding cycle were introduced, material changes were made and a post moulding annealing process was used to produce items that were resistant to cracking and fracture by zinc chloride solution. The manufacturer has now introduced stress cracking tests using zinc chloride as a standard quality control procedure for nylon 6 components.

7.2 Mechanism of Stress Cracking

7.2.1 Metal Halides

In collaboration with G.F. SANSOM, a basic study was undertaken on the mechanism of stress cracking of polyamides by metal salts. The rate of cracking of nylon 6, 66, 610 and 11 in contact with drops of a metal halides was measured under carefully controlled experimental conditions. The technique involved the use of strips of nylon (150 mm x 25 mm x 3 mm) held horizontally under stress in a tensile testing machine fitted with a Phillips pick-up, by means of which the stress could be continuously recorded. From the stress-time curve, factors such as crack initiation time, crack-through time, time to rupture and crack-through propagation period, were determined. Details of the experimental procedure are given in Part I of a series of papers by Dunn and Sansom (21.7) (Appendix 16a, p. 1642). The type of cracking observed is shown at Appendix 16a (Fig. 3, p. 1644). An enlargement of the original figure is given at Appendix 16b.

The original cracking pattern was obtained, in 1968, using nylon 6, at 21°C, and a stress of 13.79 MPa (2000 psi). Nigrosine G140 dyestuff was added to the 80% zinc chloride solution in order to clearly indicate the pattern of stress cracking and the extent of diffusion of the solution into the nylon. Nigrosine G140 is a sulphonated aniline derivative (sodium salt), known also as CI Acid Black 2. The coloured zinc chloride solution had excellent long-term storage stability. As shown at Appendix 16b, cracking occurred in the axial direction to the applied stress with propagation in a somewhat random manner from the crack tips. The rate of cracking was rapid.

In February 1978, the stress cracking of nylon 6 using 80% zinc chloride was repeated. An Amsler horizontal tensile testing machine of

200 pounds force maximum capacity was used. Nylon strips, 150 mm x 20 mm x 3 mm were maintained at a temperature of 22°C and a stress of 11.72 MPa (1700 psi). The stress cracking pattern caused by a single drop of 80% zinc chloride solution coloured with Disulphine Blue CN is shown at Appendix 16c. Disulphine Blue CN is the sodium salt of the oxidized condensation product of 4-formyl-m-benzene disulphonic acid and N,N' diethylaniline, and is also known as CI Acid Blue 1, No. 42045. The coloured solution also had excellent long-term storage stability.

An interesting comparison is the stress cracking pattern of nylon 6 caused by saturated chromic chloride compared to that produced by zinc chloride. With the former agent, slow cracking with elegant symmetrical crack propagation was observed, as shown at Appendix 16d. The area of contact of the original drop of chromic chloride is visible together with the small drops of cracking agent that were expelled from the cracks when the applied stress was removed and the nylon contracted to an equilibrium state. The pattern (Appendix 16d) was obtained after 4 hours using one drop of saturated chromic chloride solution on a nylon strip maintained at 22°C and a stress of 27.6 MPa (4000 psi). The rate of cracking under the conditions of high applied stress was slow.

The stress cracking of nylons by metal halides was found to be dependent on the concentration of the stress cracking solution, the moisture content of the nylon, the level of applied stress and the temperature. High values of these factors favoured rapid cracking. The type of nylon surface to which the stress cracking solution was applied did not markedly influence the rate of cracking. Viscosity and hardness measurements indicated that very little chemical degradation occurred when nylons were ruptured by zinc chloride.

Zinc chloride when dissolved in methanol was found to be an extremely active stress cracking reagent (Appendix 16a, p. 1651). Using crack initiation time data for nylon 6 in contact with methanolic or aqueous zinc chloride, we found that a minimum stress level of about 5 MPa was required before stress cracking could be initiated. Since injection moulded nylon components were also rapidly cracked by solutions of zinc chloride, it was most probable that these components had internal stresses of a high order. The level of internal stress in mouldings could thus be estimated by determination of the time to rupture when in contact with zinc chloride solution under standard conditions (Section 7.1 and Appendix 15e).

The results of this study indicated that stress cracking of nylon 6 by metal halide solutions was not a function of hydrogen ion concentration or involved hydrolysis or metal-ion catalysed hydrolysis. We believed the stress cracking mechanism involved reactions between the metal halide and the nylon, and these were further investigated.

7.2.2 Mechanism of failure

In Part II of our studies (218, Appendix 16e) the action of metal halides on nylon 6 and secondary amide model compounds was investigated using infrared and NMR techniques. For infrared studies biaxially stretched, extruded, blown, unplasticised nylon 6 film was mounted on a glass former that could be placed directly in the sample compartment of a spectrophotometer. Nylon 6 films produced by casting and which contained selected metal salts, were also used.

Detailed infrared studies showed that active metal halides could be divided into two groups, according to the modifications they induced in the spectra of nylon 6 films, namely:

Type I: Chlorides of zinc, cobalt(II), copper(II), iron(III), chromium(III) and manganese(II).

Type II: Chlorides of lithium, magnesium and calcium and lithium bromide.

Basically, cast nylon 6 films containing Type I metal halides all gave spectra with a characteristic new absorption band at about 1595 cm^{-1} which was not present in nylon films containing Type II metal halides. Type II halides caused the formation of a broad band in treated nylon films at about 2400 cm^{-1}, but Type I halides did not.

The spectral changes observed with nylon 6 and model compounds when treated with metal halides appeared to be due to the formation of complexes between the amide group and the halide, and structures for these complexes were proposed (Appendix 16e, p. 1669). Type I metal halides formed complexes in which the metal atom was coordinately bonded to the carbonyl oxygen atom of the amide group. These agents caused stress cracking by interferring with hydrogen bonding in the polyamide. Type II metal halides in solution formed proton donating, solvated species which could act as direct solvents for nylon 6 in a manner similar to phenols and formic acid. These agents appeared to cause simple solvent cracking.

7.2.3 Metal thiocyanates

From these studies, it was predicted that metal thiocyanates should be active stress cracking agents for polyamides. Studies confirmed these predictions and were reported as Part III of the series of papers (219, Appendix 16f).

A new simple technique was developed to rapidly assess the effects of metal thiocyanates on stressed nylon film. The film was supported over a glass annulus and stressed by the application of a reduced pressure on one side. The tensile stress at the centre of the film was calculated using Roark's equation (220). This technique gave information on the cracking activity of dilute solutions which could not be obtained using bulkier specimens. Details of the equipment are given at Appendix 16f (p. 1674).

Following the publication of this technique, instrumented equipment was constructed by Ministry of Defence, Britain for use in studies on the weathering of plastics films (221). The equipment has been in use (222) at JTTRE, Department of Defence, Innisfail, Queensland for some years.

The determination of the stress cracking properties of a number of metal thiocyanates showed that lithium, zinc and cobalt(II) thiocyanate were the most active. Their activity was compared to that of the metal halides. The mechanism of cracking was studied using infrared techniques and it was shown that the action of metal thiocyanates on nylon 6 was similar to that of the corresponding metal halides. In particular, zinc thiocyanate and cobalt(II) thiocyanate appeared to be Type I cracking agents and acted in a manner similar to the Type I metal halides described at Appendix 16e.

Calcium, lithium and barium thiocyanates appeared to be Type II cracking agents, and thus were effective solvents for nylon, their solvent power being determined by the acid strength of the solvated metal ion. Some cobaltothiocyanates were also active stress cracking agents, but these did not appear to act as Type I agents. This was not unexpected since in these compounds the cobalt(II) atom was fully coordinated in the anion. It was proposed that these agents interfered with hydrogen bonding between polymer chains by simple ionic charge effects. All our results indicated that metal thiocyanates and the corresponding metal halides promoted stress cracking in polyamides by similar mechanisms.

In 1975, Hannon and Wissbrun (223) of Celanese Research Company, described the interaction of inorganic salts with polar polymers, in particular, the physical properties of mixtures of *Phenoxy* polymers (linear condensation product of 2,2-bis(4-hydroxyphenyl)-propane (Bisphenol A) and 1-chloro-2,3-epoxy propane (epichlorohydrin)), and calcium thiocyanate. Their work confirmed some of our observations (Dunn and Sansom, 219) for reactions between metal thiocyanates and polyamides.

7.2.4 Metal nitrates

Research undertaken on metal thiocyanates resulted in further detailed studies on the effects of aqueous and non-aqueous solutions of metal nitrates on polyamides. Using standard stress cracking factors, the activity of metal nitrates was in the decreasing order:

Copper(II), zinc, cobalt(II), nickel(II), magnesium, calcium and lithium.

With the exception of the latter three metal nitrates, all were more active in aqueous solution than in methanolic solution.

Studies using infrared techniques were undertaken on the sorption of metal nitrates by nylon 6 films in order to determine the fate of the metal ion within the polymer structure. Nitrates of Type I metal cations became coordinated by the cation, despite their non-coordinated state in the aqueous solution from which they were sorbed. Nitrates of Type II cations remained uncordinated on sorption with the nylon. This type of behaviour was strong confirmation of the proposal (218) that, in their interactions with polyamides, coordination of the cation was usual with Type I agents, but not with Type II agents. This work (224) formed Part IV of the series of papers and is reproduced at Appendix 16g.

The public disclosure of our work attracted interest from other research groups in Australia. Discussions were held with staff of the Chemical Engineering Department, Materials Science Group, University of Adelaide and they initiated work on selected aspects of the stress cracking of polyamides. This resulted in the completion of a thesis by Burford (225) for the degree of Doctor of Philosophy entitled, *The Morphology of Salt-Induced Stress Crazing and Cracking in Polyamides*. Burford investigated cracking in polyamides induced by aqueous zinc chloride, cobalt chloride, magnesium perchlorate and lithium salts. Studies were also undertaken on the morphology of ruptured nylon and on mechanical and chemical aspects of stress cracking. Recently, Reimschuessel and Kim (226) have reported further work on the stress cracking of nylons induced by zinc chloride

solutions. In their studies, techniques similar to those reported by us a decade ago were used.

Work undertaken at MRL on rupture of nylons has indicated the importance of being able to monitor the susceptibility to failure in service, of moulded plastics components due to stress cracking. Typical solvent systems used at MRL to assess the stress crack resistance of selected engineering-type plastics, include: polyamides, 80% aqueous zinc chloride; polycarbonate, ethylene dichloride vapour; cast acrylic sheet, chloroform; polystyrene, kerosene; and acrylonitrile-butadiene-styrene (ABS) copolymer or polymer blend, glacial acetic acid or aniline.

7.3 Applications Resulting from Stress Cracking Observations

As described in Section 7.2 (Appendix 15e), measurement of stress crack resistance of moulded plastics components can be used to assess the extent of inbuild stress. Selected solvent systems used under carefully controlled conditions are suitable for quality control purposes.

In our studies on the action of zinc chloride on nylon, we observed using scanning electron microscopy that a fine microetched surface on the nylon could be obtained. As such a surface could provide an excellent physical key for adhesive bonding and the adhesion of surface finishes, investigations were undertaken with G.F. SANSOM (227) on the surface treatment of nylons for adhesive bonding. The work was presented at a conference in Sydney, Australia in 1969 and is reproduced at Appendix 17a.

A recommended etching agent for nylon prior to adhesive bonding is 80% by weight, of phenol and 20% by weight, of deionized water used at temperatures between 20° and 40°C (228). We found using 80% zinc chloride, that for nylon 6 there was a critical stress level of about 5-8 MPa below which stress cracking did not occur. For nylon, with stresses below the critical level, immersion in stress cracking solution at temperatures up to 50°C for periods up to 60 minutes followed by washing, produced a fine microetched surface. Suitable aqueous or methanolic-based etching solutions were zinc chloride, calcium chloride, magnesium perchlorate, zinc thiocyanate, copper nitrate and lithium chloride. Trials using epoxy based adhesives as well as cyanoacrylate adhesive, showed that etching of the surface gave adhesive bond strengths up to 300% greater than those achieved with unetched surfaces (Appendix 17a, Tables 3,4 and 5).

The treatment of nylon 6 with metal salt solutions was also found to give improved adhesion of lacquers as measured by their resistance to flex cracking (Appendix 17a, Table 6). This observation could lead to improved and more durable finishes for nylon-based plastics components.

In 1971, BASF Australia Ltd issued a data sheet on the bonding of nylon (Ultramid) using an adhesive system based on calcium chloride, water, methanol, and powdered nylon (229). Details are given at Appendix 17b. We were informed by BASF Australia Ltd that this development resulted from the public disclosure at AUSPLAS 69, Sydney (227) of our work on adhesive bonding of nylon using etching solutions.

8. NEW SEALS FOR NYLON COMPONENTS

Following our investigation of stress cracking of nylon in military telephones, we initiated the development of new elastomeric seals for use throughout the equipment.

Prototypes items contained fifteen rubber components such as "O" rings, gaskets and diaphragms. These were made from silicone or polychloroprene rubbers of different hardness grades. During manufacture, assembly, testing and reconditioning, difficulties were encountered with several of the components. Major requirements were good resistance to compression set and to embrittlement at low temperature. Minor requirements were resistance to mechanical damage and to silicone lubricants used during assembly and operation. In conjunction with T. LIGGINS an investigation was undertaken on the development of new, high-performance sealing rubbers. The cover and contents pages of the report (230) on this work, are given at Appendix 15d.

Natural rubber and polychloroprene rubber when suitably compounded provide excellent resistance to compression set and some resistance to low temperature embrittlement. However crystallization causes both these rubbers to stiffen markedly over the temperature range 0° to $-20^{\circ}C$. Although natural rubber and polychloroprene rubber components had good tensile strength and compression set characteristics, they all lacked sufficient flexibility at $-20^{\circ}C$ to function satisfactorily. Even the incorporation of butyl carbitol formal and dioctyl sebacate, as low temperature plasticisers, did not produce vulcanizates with adequate low temperature performance.

This deficiency was avoided by the use of some special silicone rubbers. However, silicone rubbers are not as resistant to silicone

lubricants as are hydrocarbon rubbers and the latter also have superior mechanical properties. The opportunity was therefore taken to investigate the use of the newly introduced ethylene-propylene copolymer rubbers in the proposed applications.

Ethylene-propylene copolymer rubber (EPR) has excellent resistance to ozone and to weathering; also heat resistance, low temperature flexibility and compression set characteristics are good. *Dutral* (231), the main EPR of the saturated copolymer type then available, was selected for use.

Special peroxide-cured formulations were developed for ethylene-propylene copolymer vulcanizates in two hardness grades (IRHD; 65 and 43) and these incorporated a low volatility, paraffinic oil plasticiser and included triallyl cyanurate (232, 233) to reduce compression set. Extensive assessment of performance showed that the two ethylene-propylene copolymer vulcanizates could be used for all gaskets, seals diaphragms and O-rings. Using MRL technical data, a specification was issued for the newly developed vulcanizates (234). An important feature of the specification was the use of immersion tests at elevated temperature (with tritolyl phosphate fluid) in order to control the quality of the ethylene-propylene copolymer vulcanizates.

Details of formulations, assessment procedures and specification requirements have been published (230).

These components for military telephones were the first applications, in Australia, for ethylene-propylene copolymer rubbers. Because of their historical interest and the lack of information on formulations and properties, details of the vulcanizates are given at Appendices 18a and 18b.

9. SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPDM) RUBBERS

Following the successful introduction of ethylene-propylene copolymer rubbers into Australia (Section 8), the opportunity arose to undertake detailed investigations into the military potential of ethylene-propylene diene (terpolymer) rubbers. This work was undertaken in 1964-65, during a period of secondment to US Army Natick Laboratories, Natick, Massachusetts.

Ethylene-propylene diene (EPDM) rubber is a terpolymer of ethylene, propylene and an unconjugated diene. It differs from ethylene-propylene copolymer rubber (EPR) in that pendant unsaturation introduced by

the diene monomer enables the rubber to be crosslinked by conventional sulphur vulcanizing techniques, as well as by organic peroxides.

EPDM rubber became commercially available in the USA in 1964, and McCabe (235) reported on compounding studies using carbon black as the reinforcing filler. The main thrust of the development of carbon black-reinforced EPDM rubbers was the promotion of high usage outlets associated with the vehicle industry for example; tyres, hoses, sealing strips and gaskets. Thus, black vulcanizates of high modulus and tensile strength were produced very early in the commercial exploitation of these rubbers.

In applications where low cost, non-black colour or good electrical resistance is required mineral fillers are used. However, in 1964, limited studies showed that poorly reinforcing mineral fillers and amorphous EPDM rubber yielded vulcanizates which did not have the excellent stress-strain properties of compounds reinforced with carbon black.

A major requirement for rubbers for military use is good resistance to long-term ageing in adverse environments. The chemical nature of the EPDM polymer indicated that, in suitably compounded formulations, it should have excellent long-term ageing characteristics. Work was therefore initiated, the aim of which was the development of high performance, silica-reinforced, non-black EPDM vulcanizates with good long-term ageing properties.

The work, which was undertaken in collaboration with V.S. JAVIER, was reported by the US Army, in 1965. Because of present limited availability, the report is reproduced in full at Appendix 19a (236). Preliminary investigations by others had shown that only fine particle size silica had a reinforcing effect in EPDM rubbers equal to that of carbon black. Detailed studies were thus required to develop curing systems for silica-reinforced EPDM rubbers that were suitable for industrial use and gave vulcanizates with the required properties.

The comprehensive review by Bachmann and coworkers (237) described the properties and reinforcing action of commercially available silica and silicates. Using fine particle size, hydrated silica (237, Hi-Sil 233) and commercial EPDM rubbers, studies were undertaken on sulphur curing systems, including the effect of "ultra" accelerators and peroxide curing systems. In order to obtain vulcanizates with high tensile strength and acceptable curing characteristics, the technique of hot-milling the filler into the rubber polymer was developed. As part of this work studies were undertaken on the effect of heat promotors (for example, p-quinone dioxime),

plasticisers for EPDM rubbers, the effect of silica activators and stearic acid, and the use of special additives, for example polar rubbers such as chlorosulphonated polyethylene and other organic compounds containing chlorine. Recently Gan, Soh and Ong (238) have studied the vulcanization of butyl rubber by p-quinone dioxime in the presence of chlorine compounds and have suggested chemical reactions for the vulcanization steps. It is likely that the mechanisms proposed would also apply to the vulcanization of EPDM rubbers by p-quinone dioxime.

Following the development of suitable formulations, investigations were undertaken on the effect of level of silica reinforcement on vulcanizate properties, the use of mixed fillers, the comparison of silica and carbon black as reinforcing agents and the use of blends of EPDM rubbers with other elastomers. Evaluation of vulcanizates included studies on the effects of high and low temperatures, ozone, chemicals, fuels, fungi and weathering. Expanded silica-reinforced EPDM rubbers were also developed. Details are given at Appendix 19a.

In this investigation some special vulcanizates were prepared in order that long-term indoor and outdoor ageing studies could be undertaken. Using optimum formulations, six non-black, silica-reinforced EPDM vulcanizates were produced (September 1964). For comparison, a nitrile-poly(vinyl chloride) rubber of known performance was also included. Laboratory records are reproduced at Appendix 19b (19.55) together with details of formulations (19.58). Following evaluation in the USA, the vulcanizates were returned to MRL, Australia for long-term ageing studies. Results of tests after indoor storage for six and thirteen years are given at Appendix 19c.

Specimens were recovered from the tensile test pieces and mounted for record purposes in order that future hardness values might be determined. For convenience, the specimens are located at the back of the thesis (Appendix 28b) together with a summary of hardness data (Appendix 28a). A suitable instrument for measuring the hardness of these mounted specimens is the Rex Durometer, Type A (239).

Experience has shown that a major problem with rubbers for military use is their inability to retain adequate elasticity during long periods of storage. The results reported at Appendices 19b and 19c indicate that non-black, silica-reinforced, EPDM vulcanizates have excellent long-term indoor ageing characteristics. A nitrile-PVC vulcanizate stored under the same condition showed marked changes in hardness with resultant loss of elasticity. By continually monitoring these specimens it will be

possible to acquire further general data on their long-term ageing characteristics.

This work supports similar work being undertaken by the British Rubber and Plastics Research Association in Northern Australia at the Joint Tropical Trials and Research Establishment, Department of Defence and in England, at Shawbury, on the long-term ageing properties of plastics and natural and synthetic rubbers. Moakes (240, 241), and Morrell and Watson (242) have recently reported some results of this work. Our work on the ageing of rubber O-rings (including ethylene-propylene terpolymer systems) under long-term compression (Section 5.9.4) is also relevant.

We believe the specimens at Appendix 28b are probably the oldest non-black, high quality EPDM rubber vulcanizates in existence. Tensile data at Appendix 19c indicates that excellent properties are retained and are similar to what could be achieved if carbon black had been used as the reinforcing filler. In addition, all the vulcanizates have remained free from surface bloom. With these vulcanizates no antioxidants or antiozonants were used, and should additional long-term protection be required, suitable additives could be included.

Results have confirmed our earlier work (236) on the performance of silica-reinforced, EPDM rubber vulcanizates. By the use of special additives, such as p-quinone dioxime and polymers or organic compounds containing chlorine, as well as processing techniques such as hot milling, high quality, non-black vulcanizates can be produced. Vulcanizates based on EPDM rubbers have many attractive properties that encourage their use in specific military applications.

10. THE TROPICAL DETERIORATION OF RUBBER

Because of the continuing need for high quality, black and non-black, rubber vulcanizates for military use, extensive weathering trials were conducted on ethylene-propylene diene elastomers as well as on vulcanizates based on SBR and nitrile-poly(vinyl chloride). This work was undertaken in the late 1960's about the same time as Bergstrom (243) was conducting similar experiments on behalf of US Army.

Vulcanizates selected for the programme were based on silica-reinforced EPDM rubbers developed by the author (Section 9) for long-term indoor ageing studies. Included for comparison, was a black silica-reinforced SBR rubber containing EPDM as an extender, a peroxide-cured EPDM rubber and a silica-reinforced, nitrile-poly(vinyl chloride) rubber that had been extensively used in the production of military components (Section 14.1).

The exposure programme was conducted at various sites in Australia, the effort being concentrated at the Joint Tropical Research Unit (JTRU), Innisfail and Cloncurry, North Queensland. The initial phase was completed in early 1968 and reported at the First Australian Rubber Technology Convention, Terrigal, New South Wales (244). A reprint of the paper appears at Appendix 20a. Included is a brief history of JTRU which is now operated in Australia by Department of Defence, as part of the Joint Tropical Trials and Research Establishment.

Following this initial phase, the trial was continued for a period of four years and included seawater immersion and soil burial. The cover and contents pages of the final report are given at Appendix 20b (245).

The results obtained on vulcanizates which were exposed after indoor storage for a total period in excess of that generally recommended for natural rubber, confirmed that end-items made from vulcanizates based on EPDM rubbers were suitable for general-purpose military use. EPDM rubber also had a beneficial effect on the outdoor weathering of SBR vulcanizates exposed under stress. With the exception of unmodified SBR vulcanizates, all specimens retained acceptable levels of physical properties following indoor storage and outdoor exposure.

White-coloured vulcanizates showed the greatest change in physical properties after outdoor exposure, but even the use of three parts of carbon black per hundred of rubber was effective in protecting silica-reinforced EPDM vulcanizates from serious degradation due to sunlight. To provide maximum protection, reinforcement with carbon black is recommended for vulcanizates that are likely to be subjected to severe weathering conditions.

The best retention of physical properties following all conditions of exposure was obtained with peroxide-cured EPDM vulcanizates. For all specimens, the effect of soil burial and water immersion was less rigorous than other exposure conditions.

Results indicated that rapid degradation of vulcanizates occurred when specimens were exposed in a stressed condition. Exposure under dynamic conditions should be even more effective in assessing environmental degradation. Although new grades of EPDM rubbers with faster rates of cure are now available, the outdoor weathering resistance of these rubbers should not be adversely affected by chemical modifications

of the base polymer.

Data now available (244, 245) should enable correlation of performance of vulcanizates with prediction of shelf-storage life from accelerated tests such as those described by Thomas, Sinnott and Day (246).

11. DEVELOPMENT OF MAGNETIC RUBBER

Magnetic polymeric compositions are used to advantage in such diverse applications as sound recording tapes, magnetic seals, brakes and clutches, magnetic switches, gaskets and latches, TV deflection yokes, reed switches and relays, in small direct-current electric motors, and in memory units of electronic computers (247-249). The first patents (250) concerning these materials were taken out in 1936, although most of the development has occurred in recent years.

In 1970, only ceramic ferrites were manufactured in Australia, using imported raw materials. However local mining developments encouraged the use of local raw materials in the production of ferrites. In cooperation with Plessey Rola Pty Ltd, Magnetic Materials Unit, Noble Park, Victoria, an investigation was undertaken, the aim of which was to develop a magnetic rubber based on the use of an Australian-produced ferrite. Plessey Rola Pty Ltd manufactured the ferrites and assisted with magnetic testing. MRL was responsible for research on the rubber-based compositions, and for the examination of the ferrites and the magnetic rubbers by means of electron microscopy.

The programme was undertaken in collaboration with J.M.D. WOODFORD, and the title and contents pages of the report of the work (251) are given at Appendix 21a. In 1978, the report was made available for public release.

When a magnetisable material is placed in a magnetic field the magnetism induced in it by the field can be described by plotting a magnetisation curve (252, 253), such as shown at Appendix 21b. The product of the flux density and the related negative applied field strength at any point of the hysterisis loop (energy product, BH) gives a measure of the energy stored within the magnet at that point. The graph of energy product BH, plotted against either the flux density (Appendix 21c) or the negative field strength over the range of the demagnetisation curve, possesses a maximum. This maximum energy product (BHmax; units, gauss oersted or tesla ampturns/m) is a good criterion of the quality of a permanent magnet. Hysterisis loops of large area, such as shown at Appendix 21b, signify permanent, or 'hard', magnets. This type of

magnet was the only one considered in the investigation.

There are two ferrites most suitable for use in permanent magnetic compositions: barium ferrite, $BaFe_{12}O_{19}(BaOFe_{12}O_{18})$ and strontium ferrite, $SrFe_{12}O_{19}(SrOFe_{12}O_{18})$. Both are manufactured by similar processes, although the strontium ferrite is more expensive due to the cost of the strontium-based raw materials. Both ferrites are fine, clinging, brown powders, when in the form used in flexible magnets. The structure and properties of ferrites have been studied in detail (254) and scanning electron micrographs of an Australian-produced ferrite are shown at Appendix 21d.

To produce satisfactory flexible magnets, the rubber must be extruded as strip or calendered as sheet and magnetized in bulk before cutting into pieces. Edwards (255) and Bowman, Skelton and Walsh (256) have described typical processes. At MRL, we used the shearing action of a two-roll, laboratory rubber mill to align the platelet-shaped ferrite particles in a uniform direction (Appendix 21e). Excellent magnetic orientation was thus obtained. Good quality permanent magnets were then produced by laminating milled sheets together. The alignment of ferrite platelets in the rubber is illustrated at Appendix 21f.

Several polymers with different chemical and mechanical properties and with differences in uncured characteristics such as "green" strength, ease of incorporation of high loadings of fillers, and flow properties during moulding , were investigated. The use of plasticisers was also investigated. Curing systems used were those conventionally employed for each elastomer. Curing and processing aids were kept to a minimum, in order to maintain the highest possible loadings of ferrite. The best polymers for use were found to be polychloroprene and butadiene-acrylonitrile. Aspects investigated included: the effect of ferrite loading and mixing techniques on magnetic properties; the effect of different elastomeric binders; the effect of particle size, particle shape and heat treatment of ferrites; and the use of strontium ferrite. Details and properties of one of the MRL-developed magnetic rubbers based on butadiene-acrylonitrile, are given at Appendix 21g (Compound W553B). The magnetic characteristics of this rubber are shown at Appendix 21c.

The results of this investigation showed that effective orientation of barium ferrite particles could be obtained by mixing the rubber-based compositions on a two-roll rubber mill. The maximum feasible loading was 66% by volume of ferrite (89 - 91% by weight), although under

these circumstances the material was rigid and fairly difficult to handle. A lower ferrite content, 60% by volume, permitted a considerable improvement in mechanical properties but slightly lowered the magnetic properties. The selection of elastomer depended on the mechanical and chemical requirements of the intended application. However, as a general rule, elastomers with high "green" strength were used in order to facilitate mixing at very high loadings.

The optimum ferrite particle size was about 1 μm and particles needed to be platelet-shaped in order to provide the required magnetic properties. This was achieved by careful control of reaction conditions for ferrite production and correct size-reduction techniques.

Annealing of ferrite powders at 950°C for one hour, improved magnetic properties by about 10 - 20%. The potential of strontium ferrite as a material for use in magnetic rubbers was also demonstrated. Information obtained on specific formulations was such that the production of high quality, flexible, magnetic rubbers using Australian ferrites is now possible.

Some details of work undertaken at MRL were described by Walsh (257) of Plessey Rola Pty Ltd at an International Defence Conference held in Canberra, Australia, in 1971. Silva and Silva (258), both of MRL, have also described scanning electron microscopy studies used in the development of magnetic rubber. Details of the formulations developed and their physical, mechanical and magnetic properties are listed in the report by Dunn and Woodford (251).

12. IMPRINTS OF BARNACLES

In Section 5.9.3 details are given of the use of organotins in the protection of timber against marine boring organisms. In this investigation some of synthetic rubber coatings were applied to treated timber panels in order to provide additional protection.

Resulting from this work was recognition of the ability of the barnacle species *Balanus amphitrite* to record their growth as imprints on a particular rubber coating based on chlorsulphonated polyethylene. The permanent set of this synthetic rubber was such that when deformation occurred as a result of pressure induced by the growing barnacle, a permanent recording of changes in the surface of the rubber resulted. This observation was investigated in conjunction with G.F. SANSOM and a draft paper prepared (259, Appendix 22a). Some of the results were

reported, in 1972, by Dunn and Sansom (184). The summary of this paper is given at Appendix 12c (p. 12.14).

In these studies it was observed that different species of *Balanus amphitrite* showed different degrees of attachment to chlorosulphonated polyethylene. Barnacle species with circular basal configurations (184, Fig. 14 and Appendix 22a, Fig. 2, top) were more easily removed from the rubber surface than those species with elliptical basal configurations (184, Fig. 13 and 14:Appendix 22a, Fig. 1 and Fig. 2, bottom). The profiles of the two types of imprints were also different. The types of profile, the chemical nature of the barnacle adhesive, and factors associated with the surface of the substrate would all be important in the determination of degree of attachment.

It is thus likely that the properties required in the rubber coating in order to permanently record growth cycle imprints were quite specific. Some details of the composition of the chlorosulphonated polyethylene coating found to be satisfactory, are given at Appendix 22b. We believe this work could be of interest to researchers concerned with studies on the prevention of marine fouling of ships and underwater structures.

13. FIRE HAZARDS OF ORGANIC MATERIALS

For many years loss of life and damage to property as a result of fire has been of concern to military, industrial and commercial authorities. During the last decade new techniques have been developed to assess the flammability and smoke generation characteristics of materials used in buildings, vehicles of all types, furnishings and clothing. Polymeric materials, in particular, have received considerable attention. Currently many research efforts are being directed to studies on the understanding of fundamental aspects of the combustion process in order that organic materials with inherent resistance to burning might be produced. These increased activities have resulted in the appearance of several new scientific journals concerned with fire, flammability and smoke (260-265). Review articles appear regularly on specialist topics, for example the fire properties of polymer-based composite materials (266).

In the early 1970's, in conjunction with J.R. BROWN, an investigation was undertaken on behalf of Navy, on the combustion of organic polymeric materials particularly the aspects of smoke generation and evaluation of flammability by the oxygen index method. Detailed reports were issued in 1973 (267, 268).

The smoke generated by a number of organic materials of interest to Navy such as, panelling materials, fire-retarded timbers, adhesives,

fibreglass laminates, cellular polymers, cable insulating materials, textiles and surface coatings, was evaluated using the Rohm and Haas Smoke Density Test Chamber. Light attenuation by smoke was measured photometrically and results reported in terms of (a) maximum smoke generation (b) maximum rate of smoke generation (c) the time period to reach an arbitrary critical smoke level and (d) the time period to reach maximum smoke generation. The title page of the report is given at Appendix 23a (267).

The oxygen index method was used to evaluate the relative flammabilities of those organic materials assessed in regard to smoke generation characteristics. The method provided a measure of the minimum volume fraction of oxygen in a mixture of oxygen and nitrogen which was capable of sustaining candle-like combustion of the material. This value constituted a convenient, reproducible numerical rating of the flammabilities of materials of interest. The title page of the report is given at Appendix 23b (268).

The two reports issued on this work were condensed into a paper by Brown and Dunn (269) which was published in 1976. A copy is given at Appendix 23c. As well as describing the techniques used for the small scale assessment of flammability and smoke generation, specific results are given for laminated materials, rigid and flexible cellular polymers, cable insulating materials and adhesives. By use of the described techniques, materials likely to be a hazard in a fire situation were identified. Important factors such as flame-spread rate, ignition temperature and heat generation, or problems associated with corrosive and toxic combustion products were not assessed. Further research on some of these aspects is currently being undertaken, independently, by J.R. Brown.

Past and present studies being undertaken at MRL on the fire hazards of organic materials should assist in the greater utilization, in military materiel, of polymers of knows safe performance.

14. MISCELLANEOUS ACTIVITIES - ORGANIC MATERIALS

14.1 Direct Moulded Soles (DMS) for Combat Footwear

During the mid-1960's the need arose for the introduction of a high performance, direct moulded sole combat boot for use by the Australian Defence Forces. The item was designed, tested and inspected by Army. Materials Research Laboratories was responsible for research and development on the rubber compound and the adhesive used for the direct moulded sole. A half section of the combat boot, showing the stainless steel anti-spike insole plate, is shown at Appendix 24a.

Using limited information available from local and overseas sources, special rubber sole and adhesive compounds were developed. The soles were based on a silica-reinforced blend of nitrile rubber and poly (vinyl chloride) with carbon black as a colouring pigment. Fungal-resistant plasticisers and vulcanizing agents were used. The compound, which was designed to have a cure time of 12 min at 160°C, also had excellent resistance to oil, flexing, weather and abrasion.

The development of this rubber has been described in detail by Dunn and Hart (270). The cover and contents pages of the report are given at Appendix 24b. Hart and others (271, 272) have described further activities undertaken, at MRL, on combat footwear. As a result of our work, a detailed specification was issued by Army (273) which included many technical aspects related to our development work. The specification is still current and present production items have components which are still based on our original developments.

14.2 Rubber and Metal *Austfire* Targets

The use of an electromechanical method of registering bullet hits on a target, known as *Austfire,* was based on the recording of the electrical pulses generated by bullet hits, or passes close to, a rubber-faced target. The electrical pulse produced by the build-up and decay of the electrostatic charge could be amplified and fed to a counter. For a near miss the pulse was about 20 millivolts, and for a hit about 500 millivolts. MRL was asked to produce a facing rubber suitable for continuous operation at any ambient temperature between -20°C and +70°C, be resistant to continuous outdoor use, have an appropriate electrical output when struck by a bullet and be resistant to serious mechanical damage as a result of bullet penetrations.

In collaboration with T. LIGGINS,a programme was undertaken which resulted in the development of a suitable rubber. The title and contents pages of the report on the work are given at Appendix 24c (274). The most satisfactory target consisted of a highly-filled, insulating, polychloroprene rubber bonded onto a perforated metal backing. The target had excellent mechanical properties when struck by bullets from the 7.62 mm SLR and developed electrical pulse outputs of about 500 millivolts. The abrasive properties of the filler used in the polymer had little effect on the amplitude of the pulse output, but the chemical nature of the filler affected the polarity of the pulse. A detailed technical specification (275) was issued, by Army, to cover the design and manufacture of rubber

and metal targets.

14.3 Rubber Plugs for Detonantless Fuzes

In the mid-1950's, a new type of detonantless fuze was developed at Materials Research Laboratories. The fuze contained a rubber component that was deformed rapidly during the functioning of the fuze.

In order to meet service requirements for an ammunition rubber, components must be non-corrosive to metals, compatible with explosives, have a long storage life and an operating temperature range of -60°C to +70°C. In conjunction with T. LIGGINS, work was undertaken on the development of suitable rubbers and assessment of performance over a wide range of conditions. The cover and contents pages of the report issued on this work are given at Appendix 24d (276).

The plugs finally shown to be satisfactory were based on a plasticised blend of natural rubber and polychloroprene. Special "sulphurless" curing systems were used in order that the vulcanizates would have long-term freedom of adhesion to, or corrosion of, copper and brass. The systems also had to have suitable curing rates for the two polymers in the blend. Although very soft rubbers were required, and were developed, production modifications were necessary in order that components could be produced by acceptable techniques.

During a period of several years, over 25000 special rubber plugs of varying designs were produced in the laboratory, and by industry, for use in detonantless fuzes.

14.4 The Weathering of Polyolefins

In the mid-1960's, polyolefins were beginning to be used in numerous military applications because of their low cost, ease of processing and ready local availability. There was, however, considerable doubt concerning the long-term resistance to weathering of polypropylenes and high and low-density polyethylenes, particularly non-black materials. Technical information on weathering had largely been generated in Europe and North America. Local experience indicated that because weathering conditions in Australia were more severe than in Europe assessment, at appropriate sites in Australia, of new materials was desirable.

In collaboration with E.J. HILL an extensive programme of work was undertaken, the aim of which was to assess the performance of several polyolefin materials under known outdoor exposure conditions. Base polymers were pigmented and injection moulded, at MRL, into suitable components for exposure. A total of twenty-three materials was exposed,

consisting of six polypropylenes, five high-density polyethylenes, five low-density polyethylenes, four low-density and high-density polyethylene blends and three poly(ethylene-ethyl acrylate) copolymers. The cover and contents page of the report by Dunn and Hill (277) on this work, is given at Appendix 24e.

Prolonged trials confirmed the efficiency of carbon black pigmentation as a suitable means of protecting polyolefins against photo-oxidation. The results shown in Table 2, Appendix 27a indicate the performance characteristics of black and natural polyolefins under tropical conditions in Australia. The relationship between change in mechanical properties (tensile strength) and time of exposure of an olive-green, low-density polyethylene is shown in Figure 2, Appendix 27a. The effect of stress in polyolefins as a result of processing by the injection moulding technique, was also observed. As shown in Figure 3, Appendix 27a, weathered specimens of low-density polyolefins showed severe cracking along stress lines induced during the moulding process. High-density polyethylenes and polypropylenes showed similar stress-cracking patterns. Stress-free materials should exhibit improved weathering characteristics.

The results of this work confirmed the importance of ultraviolet radiation as the primary cause of deterioration of unprotected polyolefins. When good weathering performance of polyolefins is required, carbon black should be used as the primary pigment. At MRL, other workers (278-280) are currently investigating the basic causes of deterioration of polyolefins by ultraviolet light. It is hoped that new techniques can be developed to improve the weathering performance of non-black polyolefins.

14.5 Other Activities

During World War II, many temporary quarters were erected in the tropics for troops and stores. These timber-framed buildings had corrugated iron roofs and walls made from paper-hessian-bitumen laminate. General deterioration made the material unsatisfactory for tropical use and a suitable substitute was sought by Army.

At MRL, work was undertaken by the author in the early 1960's on the development of a suitable plastics-based material (281). Plasticised poly(vinyl chloride) coated hessian was found to be an economical and durable replacement material that could be manufactured locally using existing equipment (282).

Colleagues at MRL have also reported other studies with which the author has been associated. In particular, Sansom (283) has described

the evaluation of environmental performance of plastics materials and mouldings. The effects of weathering in the tropics on glass-reinforced epoxy resins have been reported by Williams (284). Recently a symposium on environmental effects on advanced composite materials was held (285) which stressed the importance of this aspect to the long-term development of these materials. Some interesting observations on the adhesion of silica-reinforced, natural rubber - polyethylene laminates have recently been reported by Morris (286).

PART III. GENERAL SUPPORTING RESEARCH ACTIVITIES

As part of a special trials programme, the opportunity arose to participate in a task associated with the effects of radioactive fall-out on plants and animals. Details are given in Section 15.

Much of the applied research on organic materials described in Part II required special analytical support, particularly that based on gas chromatography and thermal methods. The availability of these techniques encouraged applied research studies on some specific problems and these are described in Section 16.

15. RADIOACTIVE ISOTOPES IN ANIMAL THYROIDS

In 1952, the successful firing occurred of the first British atomic device in the Monte Bello Islands, off the Western Australian coast. This operation led to the need to test several low yield devices on the Australian mainland. The first trials were undertaken at Emu Claypan in a remote area of South Australia in 1953. Further trials were undertaken in 1955 at a more permanent site at Maralinga, South Australia. These trials were code named, Operation BUFFALO. A photocopy of a press report of these historic trials is given at Appendix 25a.

Operation BUFFALO provided an unusual opportunity to study the effects of fallout from a nuclear explosion on pastures and grazing animals. Questions of fundamental importance included the entry of fallout in food chains, its biological availability and the extent to which it lodged on edible vegetation and entered into animal systems.

Using biological and radiobiological laboratory facilities available at the Maralinga site, investigations were undertaken by a team of scientists, on the extent and activity of fallout shortly after detonation. The results of these investigations were published in a report from the Atomic Weapons Research Establishment, United Kingdom Atomic Energy

Authority (287), in 1959. A copy of the cover page of the report is given at Appendix 25b. In 1961, the work was issued as a book edited by Loutit and Scott Russell (288). The title, contents, summary and introduction pages are given at Appendix 25c.

As part of this programme, the author was responsible for investigations on the extent to which different isotopes of iodine contributed to the dose to the thyroid of sheep soon after the detonation of a nuclear device. Fission products derived from a device exploded on the ground were obtained either as natural fallout on herbage or else on filters on aircraft flying through the radioactive cloud. The fission products were administered to sheep by various routes, and the thyroids assessed for uptake of isotopes. Details of the work entitled, *Radioactive Isotopes in Animal Thyroids*, are given at Appendix 25d.

Isotopes identified were ^{131}I, ^{133}I, ^{133}Xe, ^{135}Xe and ^{132}Te. The identification of the latter isotope confirmed the presence of ^{132}I. During the period up to four days following fission, the short-lived isotopes of xenon and iodine contributed mainly to the dose in the thyroid. For xenon however, the dose delivered to the thyroid was insignificant compared to that delivered by ^{131}I and ^{133}I. In general, the doses of the different isotopes of iodine in the thyroid agreed with the theoretically predicted figures of Dale (289). As part of the investigation, measurements were made using different types of detectors. The well-type, recording single channel γ-spectrometer set on a narrow channel to measure the maximum of the main γ-energy peak, was found to be more efficient than the standard liquid counter.

It is unlikely that the unique circumstances by which it was possible to study, in the field, the effects of fallout from a nuclear device on herbage and grazing animals, will ever be repeated.

16. ANALYSIS OF ORGANIC MATERIALS

16.1 The Determination of Pentachlorophenyl Laurate

To preserve wood used in military applications, impregnants based on a hydrocarbon solvent containing pentachlorophenyl laurate (PCPL) and dieldrin, are used. Control of the composition of the solution was usually achieved using colorimetric methods of analysis.

In conjunction with A.G. KELSO a new analytical technique for the estimation of PCPL was developed (290) using electron capture gas chromatography. The method was rapid, sensitive and able to distinguish between PCPL and sodium pentachlorophenate which was often present.

Other chlorine-containing components, such as dieldrin and DDT, could be estimated concurrently with PCPL. The paper is reproduced at Appendix 26a.

16.2 The Analysis of Fuel System Icing Inhibitors

A number of military specifications for aviation turbine fuels require the addition to the fuel of 0.10 to 0.15 per cent by volume, of ethylene glycol monomethyl ether (EGME) either alone or with small quantities of glycerol. These additives either depress the temperature at which ice crystals will form and lead to fuel system blockage or inhibit microbiological growth (291). The quantity of material so added must be determined analytically for quality surveillance purposes, the purity of the inhibitor must be ascertained, and a requirement exists for the determination of the presence of components leached out into aqueous phases present in fuel systems, on the ground and in aircraft. Chemical methods, as well as those based on refractive index, were available but these did not identify the compounds involved.

Using a combination of gas chromatographic methods, water-soluble additives which were able to partition between fuel and water phases in fuel supply systems, were identified and estimated. The reproducibility and accuracy of the methods were such that they were suitable for the quality surveillance of EGME in fuel, water in EGME, and of EGME, ethylene glycol and glycerol in water. The title and contents pages of the report on this work (292), which was undertaken with A.G. KELSO, are reproduced at Appendix 26b.

16.3 Thermal Analysis of Compounded Poly(vinyl chloride)

Poly(vinyl chloride), in different forms, is a significant polymer in many military applications, and its stability under severe environmental conditions is of importance. In conjunction with B.C. ENNIS, differential thermal analysis studies were undertaken to assess the performance of poly (vinyl chloride) containing a number of selected plasticisers. The effects of metal oxide additives, such as zinc oxide and ferric oxide, were examined in order to estimate the activation energy of the dehydrochlorination process and the relative effectiveness of the stabilizer system. The work is described in the paper reproduced at Appendix 26c (293).

16.4 The Melting of Polyacrylonitrile

About ten years ago there was some uncertainty concerning the melting point of polyacrylonitrile, because of the complex nature of the thermal decomposition of the polymer. However, when sufficiently fast

heating rates were used, differential thermal analysis allowed direct determination of the melting point of polyacrylonitrile before gross reaction occurred. Using this technique, an experimental melting point of 326°C was found, and this agreed well with predicted values. The paper describing this work, which was undertaken with B.C. ENNIS, is reproduced at Appendix 26d (294).

16.5 Identification of Acrylic Fibres

As part of our research at MRL it is often important to know the composition of commercial synthetic fibres used in military items. Using the technique described in Section 16.4, studies were undertaken with B.C. ENNIS, on the melting and decomposition of acrylic fibres when subjected to differential thermal analysis using fast heating rates. Differences in the glass transition point, melting point, and decomposition were such that the technique could be used to identify fibres of commercial origin. Details of the work are given at Appendix 26e (295).

Ennis has extended his thermal analysis studies to fibres containing chlorine (296), and with Brown (297) has also studied *Nomex* and *Kevlar* fibres. With Williams (298), he has reported on thermal analysis and dilatometry studies on cured epoxy resins.

16.6 Identification of Transparent Materials

In recent years there has been a significant increase in the use of plastics in the opthalmic industry, particularly in safety applications. Sothman (299) has described some of the more interesting advances.

At the request of several interested authorities we were asked to develop a simple identification scheme for transparent materials. In conjunction with G.F. SANSOM, the identification procedure described at Appendix 26f was developed (300). With the simple tests described, it was possible to identify transparent materials using only equipment, techniques and materials which could be found in almost any engineering workshop.

17. REVIEW ARTICLES

In order to disseminate the work of the Laboratories, review articles have been published on general subjects related to polymeric materials, as well as on specific aspects of our research programme. The former is represented by a review on plastics and metals (301) published in 1967. Significant developments in plastics materials were discussed

and forecasts made of projected developments during the next decade. In 1974, the hazards of plastics materials were reviewed (302), especially their performance in a fire situation.

Two recent reviews were associated with our research work. These are included in the Appendices as some of the figures and tables are of particular interest.

17.1 Organic Materials in Adverse Environments

As organic materials gain greater market penetration in building construction, transportation, agriculture, packaging, furniture, and domestic appliances, an increased level of performance under a wide range of environmental conditions will be required.

Tropical deterioration of organic materials, use of polymers underwater, corrosive effects of organic materials, stress cracking of organic materials and flammability and smoke-producing properties of materials, were discussed. Information was presented on the selection of organic materials for particular applications, and conclusions drawn concerning major developments to be expected in the future. The paper is reproduced at Appendix 27a (303).

17.2 Polymers in Adverse Environments

Aspects of work covered by the review included: utilization of organic materials, performance of polymers at elevated temperatures, speciality rubbers, stress cracking of polymers, flammability of polymers and the use of polymers in armour. The paper is reproduced at Appendix 27b (304).

18. CONCLUSIONS

Over a period of about twenty five years, unclassified applied research has been undertaken on organometallic compounds based on phosphorus, silicon and tin, on tetraorthoesters of titanium, on stress cracking of polyamides, on the development and application of rubber components based on ethylene-propylene copolymer rubber and ethylene-propylene diene rubber, on tropical deterioration of rubber, on magnetic rubber, on fire hazards of organic materials and on the development of specific components for military use based on polymeric materials.

As part of a major trials programme the fate, in animals, of radioactive fallout from a nuclear explosion was investigated. Analytical methods were developed for the determination of wood preservatives, and

icing inhibitors, and thermal analysis studies were undertaken on poly (vinyl chloride), on polyacrylonitrile and on acrylic fibres. Technical reviews have been presented on specific aspects of the work.

The applied research, undertaken alone or in collaboration with colleagues, has been directed towards the development of special materials and techniques for use by the Defence Forces. Organic materials with improved performance and durability in adverse environments have resulted from the work described.

19. REFERENCES

1. Gleeson, J.P. 1977. *Chem. in Aust.*, 44, 12, 307.

2. Anon. 1977. *Organic Chemistry Division. Statement of general activities.* Report OCD 77/4. Materials Research Laboratories, Department of Defence, Maribyrnong, Victoria.

3. Kosolapoff, G.M. 1950. *Organophosphorus compounds.* John Wiley and Sons Inc., New York, USA.

4. Saunders, B.R. 1957. *Some aspects of the chemistry and toxic action of organic compounds of phosphorus and fluorine.* University Press, Cambridge, Britain.

5. Heath, D.F. 1961. *Organophosphorus poisons. Anticholinesterases and related compounds.* Pergamon Press, London, Britain.

6. Rothschild, J.H. 1964. *Tomorrow's weapons.* McGraw Hill, New York, USA.

7. Clarke, R. 1968. *The silent weapons.* David McKay Company Inc., New York, USA.

8. Robinson, J.P. 1967. *Sci. J.*, 3, No. 4, 33-40.

9. Secretary-General. 1969. *Chemical and bacteriological (biological) weapons and their effects of possible use.* United Nations Publication E 69.I.24. New York, USA.

10. Consultants. 1970. *Health aspects of chemical and biological weapons.* World Health Organization, United Nations, Geneva, Switzerland.

11. Barnaby, F. 1976. *Medical protection against chemical warfare agents.* Stockholm International Peace Research Institute (SIPRI). Almquist and Wiksell International, Stockholm, Sweden.

12. Anon. 1977. *Chemical and instrumental verification of organophosphorus warfare agents.* Ministry of Foreign Affairs of Finland. The Advisory Board for Disarmament. Helsinki, Finland.

13. Meselson, M. (Ed). 1977. *Chemical weapons and chemical arms control.* American Academy of Arts and Sciences. Carnegie Endowment for International Peace, Washington, D.C., USA.

14. Lepkowski, W. 1978. *Chem. and Eng. News*, 56, No. 1, 16.

15. Hudson, R.F. 1965. *Structure and mechanism in organophosphorus chemistry. Organic Chemistry.* A Series of Monographs. Vol 6. Academic Press, London.

16. Trippett, S. (Senior Reporter) 1970. *Organophosphorus chemistry. Vol 1. A Review of the Literature Published up to June, 1969.* The Chemical Society, London, Britain.

17. Dunn, P. and Ford-Moore, A.H. 1951. *The chemistry of the alkylfluorophosphonites and related compounds. Part XXII. Isopropyl alkoxyalkylfluorophosphonites.* Porton Technical Paper No. 255. Chemical Defence Experimental Establishment, Ministry of Supply, Britain.

18. Kipping, F.S. 1937. *Proc. Roy. Soc. London*, A159, 139.

19. Burkhard, C.S., Rochow, E.G., Booth, H.S. and Hartt, J. 1947. *Chem. Revs.*, 41, 97.

20. Post, H.W. 1948. *Silicones and other organic silicon compounds.* Reinhold Publishing Company, New York, USA.

21. Rochow, E.G. 1951. *An introduction to the chemistry of the silicones.* Second edition. John Wiley and Sons, New York, USA.

22. Kirk, R.E. and Othmer, D.F. (Ed.) 1954. *Silicon compounds (organic). Encyclopedia of Chemical Technology.* Volume 12, p. 372 by Rochow, E.G. The Interscience Encyclopedia Inc., New York, USA.

23. McGregor, R.R. 1954. *Silicones and their uses.* McGraw-Hill Book Company, New York, USA.

24. Rochow, E.G., Hurd, D.T. and Lewis, R.N. 1957. *The chemistry of organometallic compounds.* John Wiley and Sons Inc., New York, USA. p.142.

25. Dunn, P. 1953. *The silicon analogues of some organophosphorus compounds.* Porton Technical Paper No. 323. Chemical Defence Experimental Establishment, Ministry of Supply, Britain.

26. Wilkins, C.J. 1951. *J. Chem. Soc.*, 2727.

27. Rosnati, L. 1948. *Gazz. chem. ital.*, 78, 516.

28. Kirk, R.E. and Othmer, D.F. (Ed.) 1954. *Silicon compounds (organic). Encyclopedia of Chemical Technology.* Volume 12. p.390. *Organosilazanes* by Rochow, E.G. The Interscience Encyclopedia Inc., New York, USA.

29. Post, H.W. 1943. *The chemistry of aliphatic orthoesters.* American Chemical Society. Monograph Series. Reinhold Publishing Company, New York. p.152.

30. Kraitzer, I., McTaggert, F. and Winter, G. 1947. *Paint Notes*, 2, 304-9 and 348-56. Department of Munitions, Commonwealth of Australia, Melbourne.

31. Kraitzer, I., McTaggert, F. and Winter, G. 1947. *J. Counc. Sci. Industr. Res. Aust.* 21, (4), 328-46.

32. Winter, G. 1953. *Esters of titanium and their use in paint. Part I: Preparation of polymeric butyl titanates; Part II: Hydrolysis and film formation and Part III: Formulation and performance of butyl titanate paints.* Report 191. Defence Standards Laboratories, Department of Supply, Maribyrnong, Vic.

33. Winter, G. 1953. *J. Oil Col. Chem. Ass.*, 36, 689.

34. Kirk, R.E. and Othmer, D.F. (Ed.). 1954. *Organic titanates. Encyclopedia of Chemical Technology.* Volume 14, p.238 by Blair, L.R., Beacham, H.H. and Nelson, W.K. The Interscience Encyclopedia Inc., New York, USA.

35. Dunn, P. 1959. *Aust. J. Appl. Sci.*, 10, No. 4, 458.

36. Mathers, A.P. and Pro, M.J. 1955. *Analyt. Chem.*, 27, 1662.

37. Bischoff, F. and Adkins, H. 1924. *J. Amer. Chem. Soc.*, 46, 256.

38. Teichner, S. 1953. *C.R. Acad. Sci. Paris*, 237, 900.

39. Ibers, J.A. 1963. *Nature, Lond.*, 197, 686.

40. Witters, R.D. and Caughlan, C.N. 1965. *Nature, Lond.*, 205, 1312.

41. Wright, D.A. and Williams, D.A. 1968. *Acta. Cryst.*, B24, 1107.

42. Dunn, P. 1960. *Aust. J. Chem.*, 13, No. 2, 225.

43. Luijten, J.G.A. and van der Kerk, G.J.M. 1952. *A survey of the chemistry and applications of organotin compounds.* Tin Research Institute, Greenford, Britain.

44. Luijten, J.G.A. and van der Kerk, G.J.M. 1955. *Investigations in the field of organotin chemistry.* Tin Research Institute, Greenford, Britain.

45. Smith, P.J. 1977. *Industrial aspects of organotin chemicals. The Organometallic and Coordination Chemistry of Germanium, Tin and Lead.* Second International Conference, 12-15 July. University of Nottingham, Britain.

46. Quarterly. *Tin and its uses.* Tin Research Institute, Greenford, Essex Britain.

47. Ingham, R.K., Rosenberg, S.D. and Gilman, H. 1960. *Organotin compounds. Chem. Revs.*, 60, 459.

48. Stone, F.G.A. and West, R. 1964 onwards. *Advances in organometallic chemistry.* Volume 1, 1964. Academic Press, New York, USA.

49. Dub. M. (Ed.) 1967. *Organometallic compounds. Methods of synthesis, physical constants and chemical reactions. Vol II. Compounds of germanium, tin and lead. Including biological activity and commercial application.* Second Edition. Weiss, R.W. (Ed.). Covering literature from 1937 to 1964. Springer-Verlag New York Inc., New York, USA.

50. Poller, R.C. 1970. *The chemistry of organotin compounds.* Logos Press Limited, London, Britain.

51. Sawyer, A.K. (Ed.) 1971-72. *Organotin compounds.* Vol 1 (1971), Vol 2 (1971) and Vol 3 (1972). Marcel Dekker Inc., New York, USA.

52. Abel, E.W. and Stone, F.G.A. 1972. *Organometallic chemistry. Volume 1. A review of literature published during 1971. A Specialist Periodical Report.* The Chemical Society, London, Britain.

53. Gielen, M. (Ed.) 1974. *Reviews on silicon, germanium, tin and lead compounds. International Quarterly Scientific Review Journal.* Vol 1, Nos 1 and 2. Freund Publishing House Ltd, Tel-Aviv, Israel.

54. Zuckerman, J.J. (Ed.) 1977. *Organotin compounds: new chemistry and applications. ACS Advances in Chemistry Series No. 157.* American Chemical Society, USA.

55. Lyle, W.H. 1958. *Brit. J. industr. Med.*, 15, 193.

56. Luijten, J.G.A. and Pezarra, S. 1957. *Brit. Plast.*, 30, No.5, 183.

57. Barnes, J.M. and Stoner, H.B. 1959. *Pharmacol. Rev.*, 11, 211.

58. Ascher, K.R.S. and Nissim, S. 1964. *World Review Pest Control*, 60, 181.

59. Barnes, J.M. 1968. *Organometallic Chem. Rev.*, 3, 137.

60. Luijten, J.G.A. 1972. *Applications and biological effects of organotin compounds.* In Sawyer, A.K. *Organotin compounds.* Volume 3, Chapter 12, p.931 (Ref. 51).

61. Sharpley, J.M. and Kaplan, A.M. 1976. *Proceedings of the Third International Biodegradation Symposium.* Applied Science Publishers Ltd., London, Britain.

62. Walters, A.H. 1977. *Biodeterioration investigation techniques.* Applied Science Publishers Ltd., London, Britain.

63. Upsher, F.J. 1977. *Methods for isolation of biodeterioration fungi and their subsequent identification.* Chapter 1, p.1 in Ref.62.

64. Kerner-Gang, W. 1977. *Evaluation techniques for the resistance of pipe-joint rings and sealants to microorganisms.* Chapter 3, p.41 in Ref.62.

65. Dunn, P. 1962. *Elastomeric and fungicidal organotin compounds.* Paper presented at ANZAAS, Sydney, Australia. 36th Congress, August.

66. Henry, M.C. and Davidsohn, W.E. 1972. *Organotin polymers.* Chap. 13, p.979 in Ref.51, Volume 3.

67. Shostakovskii, M.F. et. al. 1960. *Angew. Chem.*, 72, 1711.

68. Montermoso, J.C. et al. 1958. *Chem. and Eng. News.*, 36, No.16, 50.

69. Montermoso, J.C., Andrews, T.C. and Marinelli, L.P. 1958. *J. Polym. Sci.*, 32, No.125, 523.

70. Shostakovskii, M.F. et al. 1961. *J. Polym. Sci.*, 52, 223.

71. Neumann, W.P. 1963. *Angew. Chem.*, 2, 165.

72. Noltes, J.G. and van der Kerk, G.J.M. 1958. *Functionally substituted organotin compounds.* Tin Research Institute, Greenford, Britain.

73. Dunn, P. and Norris, T. 1964. *The preparation of organotin compounds.* Report 269. Defence Standards Laboratories, Department of Supply, Melbourne, Australia (Chem. Abs. 61, 3134g, 1964).

74. van der Kerk, G.J.M., Luijten, J.G.A. and Janssen, M.J. 1962. *Chimia*, 16, 10.

75. Luijten, J.G.A., Janssen, M.J. and van der Kerk, G.J.M. 1962. *Rec. trav.chim.*, 81, 202.

76. Abel, E.W., Brady, D. and Lerwill, B.R. 1962. *Chem. and Ind.*, 1333.

77. Gielen, M., Dehouck, C., Mokhtar-Jamai, H. and Topart, J. 1974. p.9 in Ref.53.

78. Dunn, P. and Cummins, R.A. 1963. *The infrared spectra of organotin compounds.* Report 266. Defence Standards Laboratories, Department of Supply, Melbourne, Australia. (Chem. Abs. 60, 11503f, 1964).

79. 1966. *Organometallic Grating Spectra. Organotin compounds supplied by MRL - N186K to N237K.* Sadtler Research Laboratories Inc., Philadelphia, USA.

80. Okawara, R., Webster, D.E. and Rochow, E.G. 1960. *J. Amer. Chem. Soc.*, 82, 3287.

81. Freeman, J.P. 1958. *J. Amer. Chem. Soc.*, 80, 5994.

82. Okawara, R. and Sato, H. 1961, *J. Inorg. Nucl. Chem.*, 16, 204.

83. Beattie, I.R. and Gilson, T. 1961. *J. Chem. Soc.*, 2585.

84. Poller, R.C. 1963. *J. Chem. Soc.*, 706.

85. Janssen, M.J., Luijten, J.G.A. and van der Kerk, G.J.M. 1963. *Rec. trav. chim.*, 82, 90.

86. Cummins, R.A. and Dunn, P. 1964. *Aust. J. Chem.*, 17, No.2, 185.

87. Cummins, R.A., Dunn, P. and Oldfield, D. 1971. *Aust. J. Chem.*, 24, 2257.

88. Cummins, R.A. 1964. *Aust. J. Chem.*, 17, 594.

89. Yamaji, Y., Ninomiya, K., Matsuda, H. and Matsuda, S. 1971. *Kogyo Kagaku Zasshi.*, 74, No.6, 1181.

90. Bocksteiner, G., Glew, G. and Phillip, A.T. 1974. *Elimination reactions of tributyltin w-chloroalkanoates.* Report 615. Materials Research Laboratories, Department of Defence, Melbourne, Australia.

91. Cummins, R.A. and Dunn, P. 1964. *Aust. J. Chem.*, 17, No. 4, 411.

92. Stamm, W. 1965. *Alkyltin isocyanates and isothiocyanates.* German Patent 1 206 901. Dec. 16. Stauffer Chemical Company.

93. Luijten, J.G.A., Rijkens, F. and van der Kerk, G.J.M. 1965. *Advances in Organometallic Chemistry.* Academic Press, New York, USA. Vol 3, p.397.

94. Jones, K. and Lappert, M.F. 1966. *Proc. Chem. Soc.*, 22.

95. Cahours, A. 1862. *Liebigs Ann.*, 122, 48.

96. Seyferth, D. and Rochow, E.G. 1955. *J. Amer. Chem. Soc.*, 77, 1302.

97. Seyferth, D. and Stone, F.G.A. 1957. *J. Amer. Chem. Soc.*, 79, 515.

98. Anderson, H.H. 1954. *J. Org. Chem.*, 19, 1766.

99. Anderson, H.H. and Vasta, J.A. 1954. *J. Org. Chem.*, 19, 1300.

100. Seyferth, D. and Kahlen, N. 1960, *J. Org. Chem.*, 25, 809.

101. Seyferth, D. and Kahlen, N. 1960. *J. Amer. Chem. Soc.*, 82, 1080.

102. Jenks, G.J. 1966. *The ^{15}N-^{119}Sn spin-spin coupling constant in tributyltin isothiocyanate.* Technical Note 87. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

103. Stone, F.G.A. and West, B. (Ed.). 1970. *Advances in organometallic chemistry.* Vol 9. Review by Zuckerman, J.J. *Applications of ^{119m}Sn Mössbauer spectroscopy to the study of organotin compounds.* p.22. Academic Press Inc., New York, USA.

104. Plum, H. and Runggas, F. 1974. *Use of tributyltin compounds as root-repelling compositions in sealing and filling masses based on bitumen.* Ger. Offen. 2 444 821.

105. Tsai, T.-T., Lehn, W.L. and Marshall, C.J. 1970. *J. Organometal. Chem.*, 22, 387.

106. Wiberg, N. and Joo, W.C. 1970. *J. Organometal. Chem.*, 22, 333.

107. Dunn, P. and Oldfield, D. 1971. *Aust. J. Chem.*, 24, No.3, 645.

108. Sisido, K. Nabika, K. and Isida, T. 1971. *J. Organometal. Chem.*, 33, 337.

109. Cummins, R.A. 1963. *Aust. J. Chem.*, 16, 985.

110. Cummins, R.A. 1965. *Aust. J. Chem.*, 18, 98.

111. Cummins, R.A. and Evans, J.V. 1965. *Spectrochim. Acta* , 21, 1016.

112. Russell, A.B. 1959. *Analyst*, 84, 712.

113. Mel'nikov, N.N., Ivanova, N.N. and Vladimirova, I.I. 1960. *Antiseptic protection of non-metallic surfaces.* USSR 125 325. Jan 8.

114. Mel'nikov, N.N., Andreeva, K.D., Shvetsova-Shilovskaya, S.N. and Ivanova, N.N. 1961. *Khim. Prom.*, 690.

115. Kageyama, I. and Miyamura, N. 1963. *Antifouling paint.* Brit. Pat. 917 629. 6 Feb.

116. Katsumura, T. 1962. *Nippon Kagaku Zasshi*, 83, 724.

117. Maruo, K. and Farutaka, V. 1966. *Organotin compounds.* Japan Pat. 21021.

118. Malnar, M. 1968. *Acta Pharm. Jugoslav.*, 18 (2), 65.

119. Lorberth, J. 1969. *J. Organometal. Chem.*, 17 (1), 151.

120. Dunn, P. and Oldfield, D. 1970. *J. Organometal. Chem.*, 23 (2), 459.

121. Dunn, P. and Oldfield, D. 1970. *J. Macromol. Sci.-Chem.*, 4 (5), 1157.

122. Ashley, E.C., and Nackashi, J. 1974. *J. Organometal. Chem.*, 72 (1), 11.

123. Armitage, D.A. and Tarassoli, A. 1975. *Inorg. Chem.*, 14 (5), 1210.

124. Brown, D.H., Ali Mohammed, Sharp, D.W.A. 1965. *Spectrochim. Acta* , 21 (5), 1013.

125. Herber, R.H. 1971. *J. Chem. Phys.*, 54 (9), 3755.

126. Licht, K., Geissler, H., Koehler, P., Hottmann, K., Schnorr, H. and Kriesgsmann, H. 1971. *Z. Anorg. Allg. Chem.*, 385 (3), 271.

127. Licht, K., Geissler, H., Koehler, P. and Moueller, K. 1971. *Z. Chem.*, 11 (7), 272.

128. Licht, K., Koehler, P. and Kriegsmann, H. 1975. *Z. Anorg. Allg. Chem.*, 415 (1), 31.

129. Czerwinska, E., Eckstein, Z., Ejmocki, Z. and Kowalik, R. 1967. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 15 (8), 335.

130. Czerwinska, E., and others. 1968. *Polimery*, 13 (8), 355.

131. Cardarelli, N. and Neff, H. 1970. *Biocidal elastomer compositions.* Fr. Demande. 2 011 769.

132. Ando, H. Yoshida, M. and Tanaka, M. 1973. *Organotin paste for fungicide.* Japan 73 38 847.

133. Iwamoto, H. and Kikuchi, M. 1964. *Hakko Kyokaishi*, 22 (5) 218.

134. Balandin, A.A. and Gindin, L.G. 1965. *Biofizika*, 10 (6) 986.

135. Kaplin, S. 1959. *Rodent-repelling compositions for polyethylene.* Ger. Offen. 1 915 822.

136. Nakata, T. and Kawamata, K. 1970. *Organotin-phosphorus ester catalysts for alkylene oxide polymerization.* Ger. Offen. 1 941 690.

137. Throckmorton, M.C. 1970. *Catalytic butadiene polymerization.* Fr. 584 923.

138. Byrdy, S., Ejmocki, Z. and Eckstein, Z. 1970. *Bull. Acad. Pol. Sci. Ser. Sci. Biol.*, 18, (1) 15.

139. Kanakkanatt, S.V. and Cardarelli, N.F. 1975. *Proc. Int. Controlled Release Pestic. Symp.*, 222.

140. Arndt, F. and Plum, H. 1975. *Composition with selective herbicidal and algicidal action.* Ger. Offen. 2 419 208.

141. Okumura, M., Kawashima, K., Koshiji, M. and Nishikawa, N. 1973. *Polyolefin thread for rice straw sheets.* Japan 73 04 857.

142. Nakayama, S., Nagano, Y., Aoyagi, K. and Ohbayashi, H. 1974. *Rodo Eisei*, 15, (10) 6.

143. Perkins, F. Milne, A. and Hearson, A. 1968. *Antifouling marine paint.* S. African 67 04 668.

144. Morgan, S. 1970. *Tributyltin fluoride for antifouling coatings.* Ger. Offen. 1 941 849.

145. Murayama, S., Sato, S., Ohama, Y. and Noro, M. 1970. *Ship bottom paints.* Japan 70 26 438.

146. Freiman, A. 1972. *Antifouling compositions for ship paints.* Ger. Offen. 2 222 971.

147. Skinner, Catherine E. 1972. *Biodeterior. Mater., Proc. Int. Biodeterior. Symp.*, 2nd 1971. p.456. Applied Science Publishers Ltd, England.

148. Skinner, Catherine E. 1972. *FATIPEC Congr.*, 11, 421.

149. De Nio, E.H. 1974. *Marine antifouling paints.* U.S. 3 794 501.

150. Beers, R.W. 1974. *Antifouling coating composition.* U.S. 3 801 534.

151. Neffgen, B. and Plum, H. 1976. *FATIPEC Congr.*, 13, 462.

152. Plum, H. 1976. *DEFAZET-Dtsch. Farben-Z.*, 30 (6) 264.

153. Plum, H. and Von Haaren, M. 1974. *Nonfouling plastics laminates.* Ger. Offen. 2 252 538.

154. Rascio, V.J.D., Caprari, J.J., Del Amo, B. and Ingeniero, R.D. 1975. *LEMIT An., Ser.*, 2 (3) (125).

155. Pettis, R.W., Phillip, A.T., Smith, G.C. and Wake, L.V. 1977. *Antifouling activity of phytotoxic compounds and experimental polymeric algicides.* Report 698. Materials Research Laboratories, Department of Defence, Maribyrnong, Victoria.

156. Conger, M.T. and Evans, T.A. 1974. *Antifouling composition.* U.S. 3 792 000.

157. Kitani, S., Ohhata, I. and Ninomiya, T. 1975. *Antifouling agents for marine use.* Japan 75 38 154.

158. Sheldon, A.W. 1975. *J. Paint Technol.*, 47 (600) 54.

159. Izral'yants, E.D., Kudinova, V.V. and Basova, L.S. 1976. *Lakokras. Mater. Ikh. Primen.*, (1) 11.

160. Davies, A.G. 1968. *Chem. Brit.*, 4, 403.

161. Janssen, M.J., Luijten, J.G.A. and Van der Kerk, G.J.M. 1964. *J. Organometal. Chem*, 1, 286.

162. Frankel, M., Gertner, D., Wagner, D. and Zilkha, A. 1967. *J. Organometal Chem.*, 9, 83.

163. Oldfield, D. 1970. Unpublished results. Materials Research Laboratories, Department of Defence, Melbourne, Australia.

164. Dunn, P. and Oldfield, D. 1973. *J. Organometal. Chem.*, 54, C11-C12.

165. Oldfield, D. 1975. *J. Appl. Polym. Sci.*, 19, 2911.

166. Oldfield, D. 1976. *Improved organotin polymers.* Annual Report 1975/76. Materials Research Laboratories, Department of Defence, Melbourne, Australia, p.43.

167. Morris, C.E.M. 1974. *An interferometric study of some organotin polymers.* Technical Note 338. Materials Research Laboratories, Department of Defence, Melbourne, Australia.

168. Birch, A.J. (Chairman). 1977. *Independent inquiry into the Commonwealth Scientific and Industrial Research Organisation.* Report. Australian Government Publishing Service, Canberra, Australia.

169. Jackson, R.G. and others. 1975. *Policies for the development of manufacturing industry. A green paper. Volume 1. Report to the Prime Minister by the Committee to advise on policies manufacturing industry.* Australian Government Publishing Service, Canberra, Australia.

170. 1977. *White paper on manufacturing industry.* Australian Government Publishing Service, Canberra, Australia.

171. Phillip, A.T. 1974. *Prog. Org. Coat.*, 2, 159.

172. Oldfield, D. 1973. *Proc. Roy. Aust. Chem. Inst.*, 40, 23.

173. Phillip, A.T., Bocksteiner, G., Pettis, R.W. and Glew, G.W. 1973. *Trialkyltin polymers and protective coatings containing same.* Australian Patent 56893/73. Materials Research Laboratories, Department of Defence, Melbourne, Australia.

174. de Forest, A., Pettis, R.W. and Phillip, A.T. 1975. *Elastomeric antifouling coatings after marine immersion in a tropical environment.* Technical Note 378. Materials Research Laboratories, Department of Defence, Melbourne, Australia.

175. Pettis, R.W. and Wake, L.V. 1975. *Dockyard evaluation of organotin antifouling paint for glass reinforced polyester hulls.* Technical Note 377. Materials Research Laboratories, Department of Defence, Melbourne, Australia.

176. Bocksteiner, G., Phillip, A.T. and Wake, L.V. 1976. *Organometallic polymers used in antifouling coatings for Australian waters.* Proc. 4th Int. Congress on Marine Corrosion and Fouling. No. 76/2. Juan-les-Pins, France.

177. Jackson, G.C. 1977. *Antifouling coatings based on organometallic polymers and organic biocides.* Report No. 11/77. Central Dockyard Laboratories, HM Naval Base, Ministry of Defence, Portsmouth, Britain.

178. Woodford, J.M.D. 1972. *Underwater marine coatings. Part II. Marine biocidal rubbers containing organotin toxics.* Report 496. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

179. Wake, L.V. 1973. *Underwater marine coatings. Comparison of antifouling activity of organotin compounds incorporated into nitrile rubbers.* Technical Note 316. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

180. Dunn, P. and Oldfield, D. 1975. *Rubb. Ind.*, 9 (1) 34.

181. Cardarelli, N.F. 1974. Letter dated 20 December relating to the paper, *A Novel Concept in Marine Antifouling Elastomers.* General Technology, University of Akron, Akron, Ohio, U.S.A. Reference R3/3/30, folio 93. Materials Research Laboratories, Melbourne, Australia.

182. Cardarelli, N.F. 1978. *Controlled release pesticides formulations.* CRC Press Inc., Cleveland, Ohio, U.S.A.

183. *Cascover Process. A shipworm-resistant coating system for wooden-hulled ships, based on the use of nylon cloth, glued to the hull, and protected by a paint system.* Leicester, Lovell and Co. Ltd , Southhampton, Hants, England.

184. Dunn, P. and Sansom, G.F. 1972. *Coated timber for underwater applications.* Report 498. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

185. Anon. 1957-1962. *Wood: A manual for its use as a ship-building material.* US Department of the Navy, Washington, DC, Navships Document 250-336 (In four volumes).

186. Metcalfe, C.R. and Chalk, L. 1950. *Anatomy of dicotyledons*, p.349. Oxford University Press, Britain.

187. Scurfield, G. and Silva, S.R. 1969. *Scanning electron microscopy applied to a study of the structure and properties of wood. Proceedings of the Second Annual Scanning Electron Microscope Symposium*, pp.185-196. I.I.T. Research Institute, Chicago, Illinois.

188. Scurfield, G., Silva, S.R. and Ingle, H.D. 1970. *Vessel wall structure: An investigation using scanning electron microscopy.* Report 379. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

189. Wakeman, C.M. (Chairman). 1960. *Symposium on treated wood for marine use.* American Society for Testing and Materials. *Third Pacific Area Meeting Papers.* ASTM Special Technical Publication No. 275.

190. Shapiro, H. and Frey, F.W. 1968. *The organic compounds of lead*, p.419. John Wiley and Sons, New York, USA.

191. Oldfield, D. and Sansom, G.F. 1973. *Potential antifouling coatings for timber.* Technical Note 319. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

192. Schmitt, H., Scholz, E. and Brettner, P. 1975. *Composition for protecting wood.* Ger. Offen. 2 420 235.

193. Upsher, J. 1976. *Proc. Roy. Aust. Chem. Inst.*, 43, 173.

194. Kerner-Gang, W. 1977. *Evaluation techniques for resistance of optical lenses to fungal attack.* In Walters, A.H. *Biodeterioration investigation techniques.* Applied Science Publishers Ltd, London. Chapter 7, p.105 (See Ref. 62).

195. 1971. *Special O-rings.* File R3/3/39. Materials Research Laboratories, Organic Chemistry Division, Department of Defence, Melbourne, Australia.

196. Dunn, P. and Oldfield, D. 1977. *Antifungal sealing rings - a new approach.* Report 689. Materials Research Laboratories, Department of Defence, Melbourne, Australia.

197. Dunn, P. and Oldfield, D. 1978. *Plast. and Rubb. Mats. and Applns.*, 3, No. 3, 87.

198. Paul, D.R. and Harris, F.W. 1976. *Controlled release polymeric formulations.* Symposium Series No. 33. American Chemical Society, Washington, DC, USA.

199. Heap, W.M. 1965. *Microbiological deterioration of rubbers and plastics.* Information circular No. 476. Rubber and Plastics Research Association, Shawbury, Shropshire, Britain.

200. MacLachlan, J., Heap, W.M. and Pacitti, J. 1966. *Attack of bacteria and fungi on rubbers and plastics in the tropics - a literature review.* Monograph No. 23. *Microbiological Deterioration in the Tropics*, p.185. Society of Chemical Industry, London, Britain.

201. Pacitti, J. 1965. *Attack by insects and rodents on rubbers and plastics.* Information Circular No. 475. Rubber and Plastics Research Association, Shawbury, Shropshire, Britain.

202. Pantke, M. 1977. *Test methods for evaluation of susceptibility of plasticised PVC and its components to microbial attack.* In Walters, A.H., *Biodeterioration investigation techniques.* Applied Science Publishers Ltd, London. Chapter 4, p.51 (See Ref. 62).

203. Osmon, J.L. and Klausmeier, L. 1977. *Techniques for assessing biodeterioration of plastics and plasticisers.* In Walters, A.H., *Biodeterioration investigation techniques.* Applied Science Publishers Ltd, London. Chapter 5, p.77 (See Ref. 62).

204. Verity-Smith, H. 1959. *The development of organotin stabilizers.* Tin Research Institute, Greenford, Essex, Britain.

205. Nishimoto, K. and Fuse, G. 1966. *Tin and its uses.* Tin Research Institute, No. 70, 3. Complete paper in *Mokuzai Kenkyu (Wood Research)*, No. 32, 15-26 (1964).

206. Dunn, P. and Hill, E.J. 1967. *Fungicides for use with poly(vinyl chloride).* Report 298. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

207. Dunn, P. and Hill, E.J. 1970. *Properties of weathered poly(vinyl chloride).* Report 410. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

208. Dunn, P. Oldfield, D. and Stacewicz, R.H. 1970. *J. Appl. Polym. Sci.*, 14, 2107.

209. Dunn, P., Oldfield, D. and Sansom, G.F. 1976. *Weathering of improved plasticised poly(vinyl chloride).* Paper D5. International Symposium on the Weathering of Plastics and Rubbers. The Plastics and Rubber Institute, London, Britain. 8-9 June.

210. 1962. *Provisional specification for Telephone Set K.* Army (Aust) 16G. Department of the Army. Australia.

211. 1967. *Telephone Set K (Aust), Mk2.* Specification Army (Aust) 91, Issue 9. Department of the Army. Australia

212. 1966. *Handset, Telephone, SI (Aust) No. 4A.* Specification Army (Aust) 90, Issue 3. Department of the Army. Australia.

213. Dunn, P., Hall, A.J.C. and Norris, T. 1962. *Nature*, 195, No. 4846, 1092.

214. Ensanian, M. 1962. *Nature*, 193, No. 4811, 161.

215. Rostoker, W. et. al. 1960. *Embrittlement by liquid metals.* Reinhold Publishing Company, New York, USA.

216. Dunn, P., Liggins, T. and Norris, T. 1967. *Case and seal materials for Telephone Set K. Part I. Case Materials.* Report 300. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

217. Dunn, P. and Sansom, G.F. 1969. *J. Appl. Polym. Sci.*, 13, 1641.

218. Dunn, P. and Sansom, G.F. 1969. *J. Appl. Polym. Sci.*, 13, 1657.

219. Dunn, P. and Sansom, G.F. 1969. *J. Appl. Polym. Sci.*, 13, 1673.

220. Roark, R.J. 1954. *Formulae for stress and strain.* McGraw Hill, New York, USA. p.223.

221. Cuncliffe, A.V., Davis, A. and Ledbury, K. 1975. *Artificial weathering of Epsan. A potential competitor of ABS polymers.* Technical Memo 102. Explosives Research and Development Establishment, Ministry of Defence, Waltham Abbey, Essex, Britain.

222. Pearce, P.J. 1978. *A burst test apparatus for evaluating polymers in thin film form.* Report No. 1/78. Joint Tropical Trials and Research Establishment, Department of Defence, Innisfail, Queensland, Australia.

223. Hannon, M.J. and Wissbrun, K.F. 1975. *J. Polym. Sci. Polym. Phys. Edn.*, 13, 113.

224. Dunn, P. and Sansom, G.F. 1970. *J. Appl. Polym. Sci.*, 14, 1799.

225. Burford, R.P. 1975. *The morphology of salt-induced stress crazing and cracking in polyamides.* Thesis for Doctor of Philosophy. Department of Materials Engineering, University of Adelaide, Adelaide, South Australia.

226. Reimschuessel, A.C. and Kim, Y.J. 1978. *J. Mat. Sci.*, 13, 243.

227. Dunn, P. and Sansom, G.F. 1969. *The surface treatment of nylons for adhesive bonding.* Preprint issued for AUSPLAS 69 Conference. The Plastics Institute of Australia, Sydney.

228. Snogren, R.C. 1974. *Handbook of surface preparation.* Palmerton Publishing Company Inc., New York, USA. Chapter 12, *Plastics.*

229. 1971. *Bonding of Ultramid.* Technical Data Sheet No. 441, dated June. BASF Australia Ltd, 55 Flemington Road, North Melbourne, Victoria Australia.

230. Dunn, P., Liggins, T. and Norris, T. 1967. *Case and seal materials for Telephone Set K. Part II. Seal materials.* Report 300. Defence Standards Laboratories, Department of Supply, Melbourne Australia.

231. 1963. *Dutral - general characteristics.* Bulletin DIES, N. 653-E. Montecatini, Italy.

232. Barth, H. and Peter, J. 1960. *Ethylene-vinyl acetate copolymers and their compounding.* Conference of the German Rubber Industry, West Berlin.

233. *Triallyl cyanurate.* Degussa, Deutsche Gold - und Silberscheideanstalt, 6 Frankfurt/Main, West Germany.

234. 1964. *Ethylene-propylene rubber compounds and moulded components.* Specification, Army (Aust) 100, Issue 2. Department of the Army, Australia.

235. McCabe, R.F. 1964. *Rubber Age*, 96, 397.

236. Dunn, P. and Javier, V.S. 1965. *Silica-reinforced ethylene-propylene diene (EPD) rubbers.* Report C and OM-7. US Army Natick Laboratories, US Army Materiel Command, Natick, Massachusetts, USA *(Chem Abs.* 64 6866d, 1966).

237. Bachmann, J.H., Sellers, J.W., Wagner, M.P. and Wolf, R.F. 1959. *Rubb. Chem. and Technol.*, 32, 1286.

238. Gan, L.M., Soh, G.B. and Ong, K.L. 1977. *J. Appl. Polym. Sci.*, 21, 1771.

239. 1975. *Standard method of test for indentation hardness of rubber and plastics by means of a durometer.* Standard D2240. American Society for Testing and Materials, Philadelphia, USA.

240. Moakes, R.C.W. 1975. *RAPRA Members J. (Sept/Oct.)*, 77. Rubber and Plastics Research Association, Shawbury, Britain.

241. Moakes, R.C.W. and Norman, R.H. 1977. *Long term natural ageing.* Paper presented at Conference on *Techniques for Assessing the Environmental Behaviour of Non-Metallic Materials.* Society of Environmental Engineers, Materials Group. Imperial College of Science and Technology, London. Paper 5, 27 April.

242. Morrell, S.H. and Watson, W.F. 1976. *RAPRA Members J. (May/June)*, 59. Rubber and Plastics Research Association, Shawbury, Britain.

243. Bergstrom, E.W. 1974. *Ten-year ageing of elastomeric vulcanizates in Panama, Alaska and Illinois.* Technical Report 74-038. General Thomas J. Rodman Laboratory, Department of Defense, Rock Island, Illinois, USA.

244. Dunn, P. and Hart, S.J. 1969. *Journal of the IRI*, 3, No. 2, 1.

245. Dunn, P. and Hart, S.J. 1970. *The weathering of vulcanized rubbers.* Report 408. Materials Research Laboratories, Department of Defence, Melbourne, Australia.

246. Thomas, D.K., Sinnott, R. and Day, J. 1967. *The prediction of shelf storage life in rubbers from accelerating heat ageing tests.* Technical Report 67-118. Royal Aircraft Establishment, Ministry of Defence, Farnborough, England.

247. Pacitti, J. 1963. *Magnetic polymeric compositions.* Rubber and Plastics Research Association of Great Britain, Shawbury, Shropshire. Information Circular No. 467.

248. *Plastiform.* Magnetic rubber produced by Lehman Corporation, Cincinatti, Ohio, USA.

249. Beretka, J. 1970. *Proc. Roy. Aust. Chem. Inst.*, 37, No. 6, 152.

250. Beddoes, V.J. 1968. *Patents relating to magnetic polymeric compositions.* Rubber and Plastics Research Association of Great Britain, Shawbury, Shropshire. Information Report No. 5910.

251. Dunn, P. and Woodford, J.M.D. 1970. *Development of magnetic rubbers.* Report 404. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

252. Bozorth, R.M. 1951. *Ferromagnetism.* D. Van Nostrand and Company Inc, New York, USA.

253. Sanford, R.L. and Cooter, I.L. 1962. *Basic magnetic quantities and the measurement of the magnetic properties of materials.* US Department of Commerce, National Bureau of Standards, Monograph No. 47.

254. Smit, J. and Wijn, H.P.J. 1959. *Ferrites.* Phillips' Technical Library, Eindhoven, The Netherlands. Cleaver-Hume Press Ltd, London, England.

255. Edwards, A. 1967. *Flexible magnets. Conference on Magnetic Materials and their Applications.* 26-28 September. The Institution of Electrical Engineers, London, Britain. p.51.

256. Bowman, G.G., Skelton, R.G. and Walsh, L. 1967. *Flexible anisotropic magnets.* Conference, reference 255, p.55.

257. Walsh, L. 1971. *Magnetic ceramics - a review of ferrite technology in Australia.* Paper D-5.1. *Symposium on Modern Ceramics and Ceramic Fibre Composites in Defence Applications.* Department of Defence, Canberra, Australia, 20-21 April.

258. Silva, S.R. and Silva, V.M. 1971. *Scanning electron microscopy studies in the development of magnetic rubbers.* Technical Note 196. Defence Standards Laboratories, Department of Supply, Melbourne Australia.

259. 1971. *Growth cycle imprints of barnacles.* Technical file R3/3/45. Polymers Group, Organic Chemistry Division, Materials Research Laboratories, Melbourne, Australia.

260. 1970. *Journal of fire and flammability.* Technomic Publishing Company, Westport, Connecticut, USA.

261. 1975. *Journal of Fire Retardant Chemistry.* Technomic Publishing Company, Westport, Connecticut, USA.

262. 1975. *Journal of Consumer Product Flammability.* Technomic Publishing Company, Westport, Connecticut, USA.

263. 1975. *Journal of Combustion Toxicology.* Technomic Publishing Company, Westport, Connecticut, USA.

264. 1977. *Fire research.* Elservier Sequoia, SA, Switzerland.

265. 1977. *Fire and Materials.* Heyden and Sons, Ltd., London.

266. Richardson, M.O.W. 1977. *Polymer engineering composites.* Chapter 8. Williams, J.D. *Aspects of the fire properties of polymer composites.* p.364. Applied Science Publishers Ltd, London, Britain.

267. Brown, J.R. and Dunn, P. 1973. *The combustion of organic polymeric materials. Smoke generation.* Report 560. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

268. Brown, J.R. and Dunn, P. 1973. *The combustion of organic polymeric materials. Evaluation of flammability by the oxygen index method.* Report 561. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

269. Brown, J.R. and Dunn, P. 1976. *Fire and Materials*, 1, 2.

270. Dunn, P. and Hart, S.J. 1969. *Direct moulded soles (DMS) for combat footwear. Part I. Current production.* Report 336. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

271. Hart, S.J. and Woodford, J.M.D. 1969. *Direct moulded soles for combat footwear. Part II. Development of an all-Australian sole.* Report 349. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

272. Hart, S.J. 1969. *Direct moulded soles for combat footwear. Part III. Clay loaded nitrile-poly(vinyl chloride) compounds.* Report 342. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

273. 1968. *Boot, man's, black, general service, direct-moulded sole and heel.* Specification Army (Aust) 415. Department of the Army, MGO Branch, Melbourne, Australia. Issue 3.

274. Dunn, P. and Liggins, T. 1967. *Rubber and metal Austfire targets.* Report 294. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

275. 1965. *Targets, electromechanical, target range, Austfire.* Specification Army (Aust) 130. Department of the Army, Melbourne, Australia.

276. Dunn, P. and Liggins, T. 1967. *Rubber plugs for detonantless fuzes.* Technical Note 97. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

277. Dunn, P. and Hill, E.J. 1971. *The weathering of polyolefins.* Report 421. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

278. Burchill, P.J. and Pinkerton, D.M. 1976. *J. Polym. Sci., Polym. Symp.*, 55, 185.

279. Burchill, P.J., Pinkerton, D.M. and Stacewicz, R.H. 1976. *J. Polym. Sci., Polym. Symp.*, 55, 303.

280. Pinkerton, D.M. 1977. *Polymer photostabilization with a surface grafted screener.* Proceedings of International Symposium; The Weathering of Plastics and Rubbers, Plastics and Rubbers Institute, London, 8-9 June. Paper E4.

281. Dunn, P. 1967. *Temporary building materials for use in the tropics.* Report 293. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

282. 1965. *Cloth, impregnated, PVC-coated, hessian.* Specification, Army (Aust) 705. Department of the Army, Melbourne, Australia.

283. Sansom, G.F. 1971. *Appl. Polym. Symp.*, 17, 201.

284. Williams, J.G. 1977. *Composites*, 8, No. 3. 157.

285. Christian, J.L. and Stein, B.A. 1975. *Environmental effects on advanced composite materials. ASTM Special Technical Publication 602.* A symposium presented at the Seventy-eight Annual Meeting of the American Society for Testing and Materials, Montreal, Canada. 22-27 June.

286. Morris, C.E.M. 1978. *J. Adhesion*, 9, 101.

287. Loutit, J.F. and Scott Russell, R. 1969. *Operation BUFFALO, Target Response Tests, Biology Group. Part 5: The entry of fission products into food chains.* Report No. T57/58. Atomic Weapons Research Establishment, United Kingdom Atomic Energy Authority, Aldermaston, Berkshire, Britain.

288. Loutit, J.F. and Scott Russell, R. 1961. *Progress in Nuclear Energy. Series VI. Biological Sciences. Volume 3. The entry of fission products into food chains.* Pergamon Press, London.

289. Dale, G.C. 1955. *Safety levels for contamination from fall-out from atomic trials.* Report No. O-41/55. Atomic Weapons Research Establishment, United Kingdom, Atomic Energy Authority, Aldermaston, Berkshire, Britain.

290. Dunn, P. and Kelso, A.G. 1968. *J. Gas Chromatog.*, 6, 13.

291. Hazzard, G.F., Kuster, E.C., Lamborn, I.R. and Marson, F. 1961-67. *Fungal growths in aviation fuel systems.* Report 252, Parts I to VI. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

292. Dunn, P. and Kelso, A.G. 1968. *The analysis of fuel system icing inhibitors (FSII) based on ethylene glycol monomethyl ether.* Report 309. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.

293. Dunn, P. and Ennis, B.C. 1970. *J. Appl. Polym. Sci.*, 14, 355.

294. Dunn, P. and Ennis, B.C. 1970. *J. Appl. Polym. Sci.*, 14, 1795.

295. Dunn, P. and Ennis, B.C. 1971. *Thermochimica Acta*, 3, 81.

296. Ennis, B.C. 1977. *Thermochimica Acta*, 21, 47.

297. Brown, J.R. and Ennis, B.C. 1977. *Text. Res. J.*, 47, No. 1, 62.

298. Ennis, B.C. and Williams, J.G. 1977. *Thermochimica Acta*, 21, 355.

299. Sothman, R.D. 1977. *Proc. Roy. Aust. Chem. Inst.*, 44, No. 2, 47.

300. Dunn, P. and Sansom, G.F. 1968. *Australasian Engineer.* No. 2, Feb., 37. Reprinted in *Aust. J. Optometry*, 52, No. 2, 50 (1969).

301. Dunn, P. 1967. *J. Aust. Inst. Met.*, 12, No. 3, 234.

302. Dunn, P. 1974. *Hazards of plastics materials.* Preprint. Fourth Annual Conference of the Institution of Fire Engineers, Brisbane, Queensland, Australia. 30-31 May.

303. Dunn, P. 1971. *Organic materials in adverse environments.* Report 458. Defence Standards Laboratories, Department of Supply, Melbourne, Victoria, Australia.

304. Dunn, P. 1973. *Proc. Roy. Aust. Chem. Inst.*, 40, 65.

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APPENDIX 1 RESEARCH ACTIVITIES, 1951-78 1.2 - 1.3

APPENDIX 2 INFORMATION CONCERNING CO-AUTHORS 2.1 - 2.2

APPENDIX 1

Applied Research Activities for the Period 1951-78

Period	Location	Activities
Prior to 1951	University of Tasmania	Post graduate research on the biochemistry of cancer.
January, 1951	Defence Standards Laboratories (DSL) Department of Supply, Maribyrnong, Vic.	Prebriefing on the chemistry and applications of organophosphorus compounds. (Scientific Officer)
March, 1951 - April, 1953(a)	Chemical Defence Experimental Establishment, Ministry of Supply, England.	Applied research on organophosphorus and organosilicon compounds.
May, 1953 - June, 1956	General Chemistry Group, DSL	General analytical investigations and studies on organotitanium compounds. (Higher Scientific Officer)
July, 1956 - September, 1956 (a)	Trials Range, Maralinga, South Australia. Attached to Ministry of Supply for OPERATION BUFFALO.	Research studies on the fate of fission products from an atomic explosion on plants and animals.
October, 1956 - May, 1957	General Chemistry Group, DSL	Continuation of studies on the chemistry of organotitanium compounds.
June, 1957 - August, 1957(a)	Radiobiological Research Unit, Medical Research Council, AERE, Harwell, England.	Completion of studies initiated at OPERATION BUFFALO.
September, 1957 - February, 1964	General Chemistry Group, DSL	Initiation and conduct of applied research activities on organic materials and on the chemistry of organotin compounds. (Higher Scientific Officer, Senior Scientific Officer and Senior Research Scientist)

Period	Location	Activities
March, 1964 - April, 1965(a)	U.S. Army Natick Laboratories, Natick, Massachusetts, USA. (Now U.S. Army Natick Research and Development Command).	Studies on non-black, high performance, ethylene-propylene diene rubbers and on U.S. Army activities on plastics, rubbers and adhesives.
May, 1965 - September, 1968	General Chemistry Group, DSL	Continuation of research and development activities on organic materials and organotin compounds.
September, 1968 - September, 1975	Polymers Group, DSL (b)	Responsible for the scientific direction of Polymers Group, Organic Chemistry Division (Principal Research Scientist).
September, 1975 - July, 1976	Organic Materials Composite, MRL	Scientific direction of the Composite, involving research activities on polymers, deterioration studies, textiles and fuels and lubricants. (Senior Principal Research Scientist)
July, 1976 - present	Organic Chemistry Division, MRL	Scientific direction of the Division. (Superintendent)

(a) On secondment from Commonwealth of Australia

(b) Change of name from DSL to Materials Research Laboratories (MRL) on 19 September, 1974 and transfer to Department of Defence.

APPENDIX 2

INFORMATION CONCERNING CO-AUTHORS

Co-author	Organisation	Designation at time papers published	Present position	Present Designation
BROWN, Dr J.R.	MRL	RS(a)	Deterioration Research Group, MRL	RS
CUMMINS, R.A.	MRL	RS	General Chemistry Group, MRL	PRS
ENNIS, Dr B.C.	MRL	RS/SRS	General Chemistry Group, MRL	SRS
FORD-MOORE, A.H.	CDEE(b)	SPSO	Deceased, 1958	-
HALL, A.J.C.	MRL	PRS	Retired, 1976	-
HART, S.J.	MRL	EOII	Retired, 1977	-
HILL, E.J.	MRL	EOI	JTTRE(c)	EOIII
JAVIER, V.S.	NLabs(d)	EOII (equivalent)	USANRDC(d)	EOIII (equivalent)
KELSO, A.G.	MRL	EOII	General Chemistry Group, MRL	EOIII
LIGGINS, T.	MRL	EOII	Resigned, 1965(e)	-
NORRIS, T.	MRL	TA2/EOI	Resigned, 1965(f)	-
OLDFIELD, Dr D.	MRL	RS/SRS	Polymers Group, MRL	SRS
SANSOM, G.F.	MRL	EOII/EOIII	Resigned, 1977(g)	-
STACEWICZ, R.H.	MRL	TA2	Deterioration Research Group, MRL	EOII
WOODFORD, J.M.D.	MRL	EOI	Resigned, 1974(h)	-

Notes for APPENDIX 2

(a) Designations: SPSO, Senior Principal Scientific Officer (UK); PRS, Principal Research Scientist; SRS, Senior Research Scientist; RS, Research Scientist; EOI-III, Experimental Officer, Class I-III; TA2, Technical Assistant,Grade 2.

(b) Chemical Defence Experimental Establishment, Ministry of Supply, Porton Down, Wiltshire, Britain. Now Chemical Defence Establishment, Ministry of Defence.

(c) Joint Tropical Trials and Research Establishment, Defence Science and Technology, Department of Defence, Innisfail, North Queensland, Australia.

(d) US Army Natick Laboratories, Natick, Massachusetts, USA. Now US Army Natick Research and Development Command.

(e) Olympic General Products, Mephan Street, Footscray, Victoria, Australia.

(f) SGE Scientific Pty Ltd, 1 Baillie Street, North Melbourne, Victoria, Australia.

(g) Church of England, Melbourne Diocese, Victoria, Australia.

(h) W.A. Deutscher Pty Ltd, South Road, Moorabbin, Victoria, Australia.

APPENDIX 3 ORGANOPHOSPHORUS COMPOUNDS

3a Photocopy of the cover page of Porton Technical Paper PTP 255 (1951), Ministry of Supply, Britain. 3.2

3b The Chemistry of the Alkylfluorophosphonites and Related Compounds. Part XXII. Isopropyl Alkoxyalkylfluorophosphonites. 3.3 - 3.10
P. DUNN and A.H. FORD-MOORE

A copy of Report 255 with minor deletions and approved for unlimited distribution, was received at MRL from Defence Research Information Centre, Ministry of Defence, Britain on 10 January, 1979. The work presented at Appendix 3b is an unabridged retype of the approved report. Reports quoted (p.3.10) are not necessarily available to members of the public or to commercial organisations.

P.T.P. 255

MINISTRY OF SUPPLY

DIRECTORATE OF CHEMICAL DEFENCE RESEARCH AND DEVELOPMENT

CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT

THE CHEMISTRY OF THE ALKYL FLUOROPHOSPHONITES AND RELATED COMPOUNDS

PART XXII

ISOPROPYL ALKOXYALKYLFLUOROPHOSPHONITES

By

P. DUNN AND A.H. FORD - MOORE

PORTON TECHNICAL PAPER No. 255

C.D.E.E.
Porton.
Wilts.

3.2

Appendix 3a - Photocopy of cover page of Porton Technical Paper 255, Ministry of Supply, Britain - 1951.

APPENDIX 3b

SUMMARY OF
PORTON TECHNICAL PAPER NO. 255

COPY NO.

DATE 18 SEP 1951

THE CHEMISTRY OF THE ALKYLFLUOROPHOSPHONITES AND RELATED COMPOUNDS

PART XXII. ISOPROPYL ALKOXYALKYLFLUOROPHOSPHONITES

by

P. Dunn[x] and A.H. Ford-Moore

1. Four members of a new type of fluorophosphonite, having an ether group attached to the phosphorus atom, have been prepared.

2. Ethers containing the group -O.CHCl.R react readily with triisopropyl phosphite to give the expected diisopropyl alkoxyalkylphosphonate. Diisopropyl isopropylphosphonate is formed at the same time.

3. Phosgenation of the diisopropyl alkoxyalkylphosphonates proceeds along normal lines but the isopropyl alkoxyalkylchlorophosphonites are very resistant to fluorination.

(Sgd.) L.T.D. Williams
Head, Chemistry Section

(Sgd.) S.A. Mumford
Supt., Research Division

[x]Australian Scientist attached Chemistry Section, C.D.E.E., Porton.

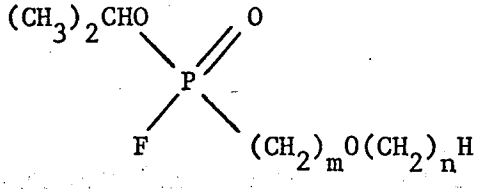
THE CHEMISTRY OF THE ALKYLFLUOROPHOSPHONITES[++] AND RELATED COMPOUNDS

PART XXII. ISOPROPYL ALKOXYALKYLFLUOROPHOSPHONITES

by

P. Dunn[x] and A.H. Ford-Moore

It has previously been noted that, among the various fluorophosphonites described in this series of reports, any alteration in the alkane[ϕ] part of the Sarin molecule leads to a considerable reduction in toxicity, in certain cases to vanishing point. It was therefore of interest to see whether a new type of substance, isopropyl alkoxyalkylfluorophosphonite (I) followed this general rule.



(I)

Four members of this series have therefore been prepared by the "Phosgene" method (1) (2). The appropriate chloroalkyl alkyl ether was made to react with triisopropyl phosphite, giving isopropyl alkoxyalkylchlorophosphonite. This was then fluorinated to give the desired compound.

Some interesting points emerge from the preparation of these compounds. An "Arbusov rearrangement" does not, as a rule, take place between trialkyl phosphites and chloro-compounds. Nevertheless, with chloromethyl (or 1-chloroethyl) alkyl ethers, no difficulty is experienced in preparing the dialkyl alkoxyalkylphosphonates by this method. The ease with which the reaction takes place recalls that between trialkyl phosphites and acetyl chloride (3). Like acetyl chloride, chloromethyl alkyl ethers contain a very reactive and easily hydrolysed chlorine atom. During the reaction, appreciable quantities of diisopropyl isopropylphosphonate (4) are formed by the action of the liberated isopropyl chloride on unreacted triisopropyl phosphite.

It is significant that 2-chloroethyl methyl ether (5), a compound in which the chlorine is much less acidic than in the corresponding 1-chloro compound, has to be converted into 2-iodoethyl methyl ether (5) before the reaction with triisopropyl phosphite will proceed.

[++] The nomenclature of the organic phosphorus compounds is in the process of review. For the purpose of continuity, that used in previous Porton Technical Papers on this subject is being maintained in the present report.

[ϕ] "Alkane" refers to that part of the Sarin molecule that contains the direct phosphorus-carbon linkage.

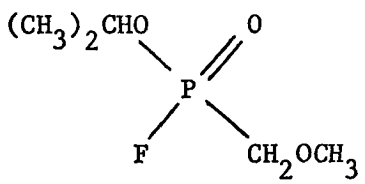
[x] Australian Scientist attached to Chemistry Section, C.D.E.E., Porton.

As will be seen subsequently, all the members of this series have a very low order of toxicity compared with Sarin. It is noteworthy that like other fluorophosphonites exhibiting a low toxicity, the chlorine in the corresponding chlorophosphonite is very resistant to fluorination. In the series of compounds under review, the chloro body is recovered unchanged after prolonged boiling with sodium fluoride in benzene suspension; fluorination can only be effected with antimony trifluoride and even then the yield of final product is poor.

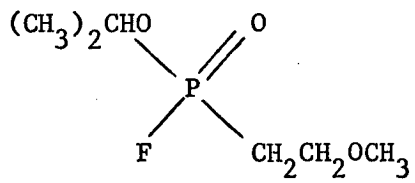
This poor yield may be in part accounted for by the fact that the corresponding chloro compounds are somewhat easily pyrolysed and their isolation can only be effected by distillation at pressures below 1 mm.

When 1-chloroethyl methylether is made to react with triisopropyl phosphite (previously distilled over sodium wire to remove any diisopropyl hydrogen phosphite[++]), several side reactions take place that further reduce the yield of product. During the reaction, the ether loses hydrogen chloride since methyl vinyl ether can be isolated. The hydrogen chloride in turn dealkylates some of the triisopropyl phosphite and considerable quantities of diisopropyl hydrogen phosphite (ca 40%) can be obtained during the final distillation. No diisopropyl isopropylphosphonate appears to be formed in this case.

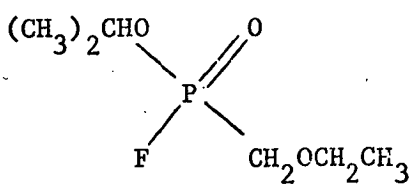
Four compounds of this type have been prepared: Isopropyl methoxymethylfluorophosphonite, T 2207 (II); isopropyl 2-methoxyethyl-fluorophosphonite, T 2208 (III); isopropyl ethoxymethylfluorophosphonite, T 2209 (IV); isopropyl 1-methoxyethylfluorophosphonite, T 2210 (V).



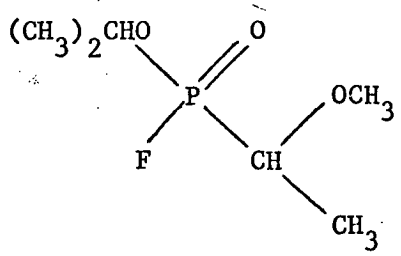
T 2207 (II)



T 2208 (III)

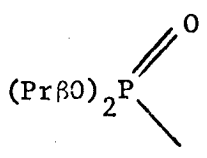


T 2209 (IV)



T 2210 (V)

[++]More correctly, diisopropyl phosphonate since it has the structure:



II

Toxicities

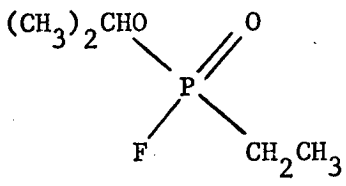
The toxicities of the above compounds (LD 50; mg/kg) are as follows:

Compound		T 2207	T 2208	T 2209	T 2210
Toxicity	Rabbits (Intrav.)	>2.0	0.22	ca 3.0	ca 0.5
	Rats (Subcut.)	-	0.8	-	>3.0

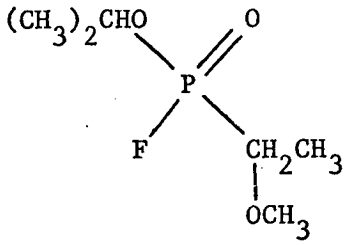
Their relative molar toxicity (R.M.T.) (Rabbits, intrav ; Sarin = 100) is therefore:

Compound	T 2207	T 2208	T 2209	T 2210
R.M.T.	>1.2	ca 10	ca 0.9	ca 5

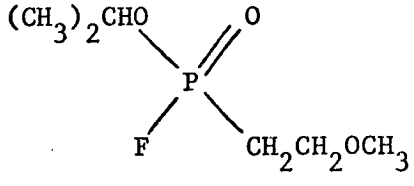
The reduction in toxicity on introducing ether groups into Sarin and T 2109 is remarkable, though this reduction is much less marked in the latter substance when the substitution is on the β-carbon of the ethyl group:



T 2109
R.M.T. ca 40

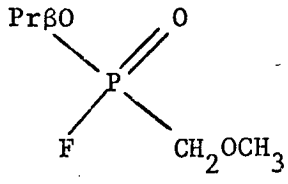


T 2210
R.M.T. ca 5

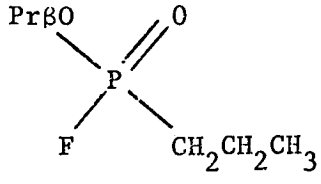


T 2208
R.M.T. ca 10

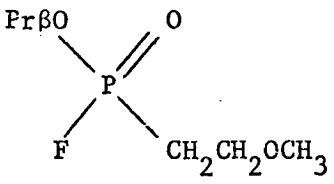
If T 2207, 2208 and 2209 be regarded as derivatives of T 2119 and 2120, a methylene of which is replaced by oxygen, the fall in toxicity is not nearly so marked; in fact, with T 2208, it shows an increase:



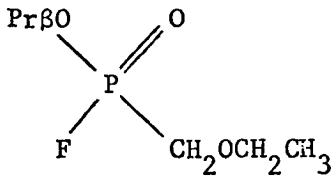
T 2207
R.M.T. >1.2



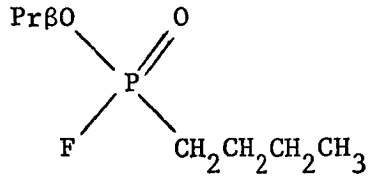
T 2219
R.M.T. 9.5



T 2208
R.M.T. ca 10



T 2209
R.M.T. ca 0.9



T 2210
R.M.T. 6.5

The most toxic member of the series is T 2208, i.e., the compound derived from by far the least acidic of the ethers.

Acknowledgements

The toxicological assessments were carried out by W/Cdr. A. Muir, R.A.F. and F. Burgess.

(Sgd.) L.T.D. Williams
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(Sgd.) S.A. Mumford
Supt., Research Division

PD/AHFM/CE

APPENDIX

Experimental

1. T 2207

(a) Diisopropyl methoxymethylphosphonate (A).

Triisopropyl phosphite (b.p.62°/11 mm; n_D^{25} 1.4084; 156 g = 0.75 mole) was heated to 100° and chlorodimethyl ether (6) (b.p.58-59°; n_D^{25} 1.3923; 68.5 g = 0.85 mole) added slowly over a period of one hour, the temperature of the reaction mixture being maintained at 100° during the addition. The reaction flask was fitted with a fractionating column and the isopropyl chloride formed allowed to distil as fast as it was liberated. At the end of this time, the temperature of the reaction mixture was raised to 140° for a further hour. The product was then fractionated under reduced pressure. After a small quantity of unchanged phosphite had distilled, diisopropyl isopropylphosphonate (4) was collected at 60-65°/1.5 mm. The yield was 18 g (10%); n_D^{25} 1.4117. Finally the product distilled at 75°/1.5 mm. It had n_D^{25} 1.4174. Yield 116 g (74%). Found C 45.75 H 9.45; $C_8H_{19}O_4P$ requires C 45.7 H 9.1%.

There was practically no residue from the distillation.

(b) Isopropyl methoxymethylchlorophosphonite (B).

(A) (67 g) was phosgenated in the usual manner (1) (7), the temperature being kept below 40° during the passage of the gas which occupied sixteen hours. After degassing, it was distilled at a pressure below 1 mm. The product had b.p. 59°/0.5 mm; n_D^{25} 1.4361. Yield 41 g (69%). Found Cl 18.65; $C_5H_{12}O_3ClP$ requires Cl 19.0%.

(c) T 2207

(B) (50 g) in benzene (100 cc.) was gently refluxed in an oil bath with antimony trifluoride (23 g; 30% excess). After filtration, the benzene was recovered and the residue fractionated under reduced pressure. The product had b.p. 52°/1.5 mm; n_D^{25} 1.3959. Yield 20 g (44%). Found C 35.3 H 7.1; $C_5H_{12}O_3FP$ requires C 34.9 H 7.3%.

Fluorination of (B) could not be effected by refluxing with sodium fluoride in benzene suspension for six hours, the starting material being recovered unchanged.

2. T 2208

(a) 2-Chloroethyl methyl ether (C).

This was prepared by the method of Jones and Powers (5) by the methylation of ethylene chlorohydrin with dimethyl sulphate. It had b.p. 90-91°; n_D^{25} 1.4070.

(b) 2-Iodoethyl methyl ether (D).

This was prepared by the method of Jones and Powers by heating (C) with excess of sodium iodide in acetone for fifteen hours. It had b.p. 56°/40 mm; n_D^{25} 1.4985.

(c) Diisopropyl 2-methoxyethylphosphonate (E).

The method of preparation was similar to that of (A); (D) (93 g = 0.5 mole) was added over one hour to triisopropyl phosphite (95 g = 0.46 mole) kept at 140° during the addition and raised to 165° for a further hour after the addition. The product on fractionating yielded isopropyl iodide, a small quantity of triisopropyl phosphite, diisopropyl isopropylphosphonate, b.p. 60-65°/1.5 mm; n_D^{25} 1.4120 (15 g = 16%), and the product b.p. 87°/1.5 mm; n_D^{25} 1.4201. Yield 70 g (69%). Found C 48.25 H 9.7; $C_9H_{21}O_4P$ requires C 48.2 H 9.45%.

(d) Isopropyl 2-methoxyethylchlorophosphonite (F).

(E) was phosgenated in the same manner as (A). The product had b.p. 65°/0.4 mm; n_D^{25} 1.4387. Yield 78%. Found Cl 17.55; $C_6H_{14}O_3ClP$ requires Cl 17.65%.

(e) T 2208

(F) was fluorinated in benzene with antimony trifluoride as for T 2207. The product had b.p. 55°/1.5 mm; n_D^{25} 1.4020. Yield 37%. Found C 39.1 H 7.95; $C_6H_{14}O_3FP$ requires C 39.1 H 7.65%.

After the distillation of the product, there was a considerable amount of clear, viscous, undistillable residue.

3. T 2209

The preparation of this compound was carried out in a similar manner to that of T 2207. The starting material, chloromethyl ethyl ether (G) (from ethanol, paraformaldehyde and hydrogen chloride) had b.p. 81°; n_D^{25} 1.3980.

Diisopropyl ethoxymethylphosphonate (H) was obtained, together with some diisopropyl isopropylphosphonate (19%) by the action of (G) on triisopropyl phosphite. It had b.p. 82°/1.5; n_D^{25} 1.4176. Yield 68%. Found C 48.3 H 9.65; $C_9H_{21}O_4P$ requires C 48.2 H 9.45%.

Isopropyl ethoxymethylchlorophosphonite (K) was prepared by the phosgenation of (H). It had b.p. 61°/0.5 mm; n_D^{25} 1.4348. Yield 70%. Found Cl 16.75; $C_6H_{14}O_3ClP$ requires Cl 17.65%.

T 2209 was prepared in poor yield by fluorinating (K) with antimony trifluoride. It was insoluble in petrol b.p. 60-80° and had b.p. 53°/1 mm; n_D^{25} 1.3974. Yield, 14%. Found C 39.0 H 7.8; $C_6H_{14}O_3FP$ requires C 39.1 H 7.65%.

A considerable amount of semi-solid residue, possibly a complex containing antimony, remained after distillation of the product.

4. T 2210

(a) 1-Chloroethyl methyl ether (L).

This was prepared by the method of Henze and Murchison (8) from paralydehyde, methanol and hydrogen chloride. It had b.p. 70-71°; n_D^{25} 1.3920.

(b) Diisopropyl 1-methoxyethylphosphonate (M).

The reaction between (L) (70g) and triisopropyl phosphite (145 g) was carried out at 80° for 15 minutes and then raised to 110°. A cold trap fitted to the top of the reflux condenser collected methyl vinyl ether (15g; b.p. 9-10°). On distillation of the residue, diisopropyl hydrogen phosphite was collected at 53°/1 mm; n_D^{25} 1.4070. Yield 45 g (39%). The product had b.p. 73°/1.5 mm; n_D^{25} 1.4167. Yield 78 g (54%). Found D 49.0 H 9.85; $C_9H_{21}O_4P$ requires C 48.2 H 9.45%.

(c) Phosgenation of (M) gave isopropyl 1-methoxyethylchlorophosphonite (N) in 72% yield; b.p. 66°/0.7 mm; n_D^{25} 1.4360. Found Cl 16.6; $C_6H_{14}O_3ClP$ requires Cl 17.7%.

(d) T 2210. was obtained in 27% yield by the fluorination of (N) with antimony trifluoride. It had b.p. 52°/1.5 mm; n_D^{25} 1.3984. Found C 38.8 H 8.1; $C_6H_{14}O_3FP$ requires C 39.1 H 7.7%.

An attempt was made to fluorinate (N) with zinc fluoride. The yield was only 10% of a sample containing some unreacted chloro compound, together with a large amount of clear, viscous, undistillable residue.

BIBLIOGRAPHY

1. Ford-Moore and Charlton; Porton Technical Paper No. 49. The Chemistry of the Alkylfluorophosphonates, Part IV. Ministry of Supply, England.

2. Ford-Moore; Porton Technical Paper No. 62. The Chemistry of the Alkylfluorophosphonates, Part V. Ministry of Supply, England.

3. Ford-Moore; Porton Technical Paper No. 169. The Chemistry of the Alkylfluorophosphonites and Related Compounds, Part XII. Ministry of Supply, England.

4. Lermit; Porton Technical Paper No. 168. The Chemistry of the Alkylfluorophosphonites, Part X. Ministry of Supply, England.

5. Jones and Powers; J. Amer. C. S. 46, 2531 (1924)

6. Organic Syntheses; Coll. Vol. I., 377

7. Perry; Porton Technical Paper No. 166; The Chemistry of the Alkylfluorophosphonites and Related Compounds, Part XI. Ministry of Supply, England.

8. Henze and Murchison; J. Amer. C. S. 53, 4077 (1931)

APPENDIX 4 ORGANOSILICON COMPOUNDS

4a Photocopy of the cover page of Porton Technical Paper, PTP 323 (1953), Ministry of Supply, Britain. 4.2

4b The Silicon Analogues of Some Organophosphorus Compounds. 4.3 - 4.39
P. DUNN

4c PTP 323 Addendum 1. Methylisocyanosilanes. 4.40 - 4.43

A copy of Report 323 (including Addendum 1) with minor deletions and approved for unlimited distribution, was received at MRL from Defence Research Information Centre, Ministry of Defence, Britain on 10 January, 1979. The work presented at Appendices 4b and 4c is an unabridged retype of the approved report. Reports quoted (p.4.38 and 4.39) are not necessarily available to members of the public or to commercial organisations.

P.T.P. 323

MINISTRY OF SUPPLY

DIRECTORATE OF CHEMICAL DEFENCE RESEARCH AND DEVELOPMENT

CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT

THE SILICON ANALOGUES OF SOME ORGANO-PHOSPHORUS COMPOUNDS

By

P. DUNN

PORTON TECHNICAL PAPER No. 323

C.D.E.E.
Porton.
Wilts.

Appendix 4a - Photocopy of cover page of Porton Technical Paper 323, Ministry of Supply, Britain - 1953.

APPENDIX 4 b

SUMMARY OF
PORTON TECHNICAL PAPER No. 323

DATE: 19 FEB 1953

The Silicon Analogues of some Organo-phosphorus Compounds

by

P. Dunn[x]

1. In addition to some previously reported silanes, twenty-three new organo-silicon compounds have been prepared and physiologically assayed.

2. The following types of compounds have been investigated:-

(a) Alkyl alkoxy chloro and fluoro silanes.

(b) Alkoxy dialkylamino alkyl chloro silanes.

(c) Alkyl and alkoxy dialkylamino silanes.

(d) Alkyl alkoxy disiloxanes and disilazanes.

3. The physiological results agree with the suggestion that the toxicity of the organo-silicon compounds reflects the toxicity of the toxic substituents.

(Sgd.) L.T.D. WILLIAMS
Head, Chemistry Section.

(Sgd.) E.A. PERREN,
Supt., Research Division.

[x]Australian Scientist attached to C.D.E.E., Porton.

PORTON TECHNICAL PAPER No. 323

DATE: 19 FEB 1953

The Silicon Analogues of some Organo-phosphorus Compounds

by

P. Dunn[x]

Introduction

Within the last decade many organo-phosphorus compounds have assumed importance due to their highly toxic properties. Thus they have proved to be powerful insecticides and to have desirable properties as potential chemical defence agents.

This report deals with the synthesis of some organo-silicon compounds, whose structure resembles somewhat, that of various organo-phosphorus compounds. In order to simulate the structure of the toxic alkyl alkyl-fluorophosphinates ("Sarins"), some alkyl alkoxy fluoro silanes have been prepared. Extension of this project to include substituted amino silanes, disilazanes and disiloxanes has yielded various new compounds.

Although many organo-silanes are physiologically inactive, the study of the toxicity of the organo-silicon nucleus is possible through the synthesis of compounds containing a toxic substituent. Due to the polysyllabic nature of the silicon nomenclature, the use of T numbers to designate particular compounds has been freely used. A list of these will be found in Table I.

Discussion

1. In order to make an arbitrary comparison of the structure of various organo-silicon and organo-phosphorus compounds, the $\equiv Si - R$ group and the $\equiv P = O$ group are considered to be structurally equivalent. Table II shows the structural comparison for nine different sets of specific compounds in which we are interested.

2. The basic set of compounds used in organo-silicon syntheses are the alkyl halo silanes, represented by the general formula (XIX). As shown in

$$Rn\ Si\ X\ (4-n)$$

(XIX)

Table II, A, they are structurally related to the alkyl phosphonyl dihalides.

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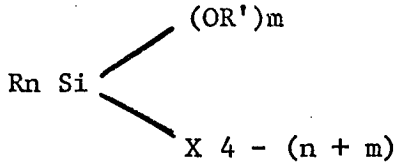
These organo-silanes are usually prepared by the action of an organo-metallic compound upon a silicon halide or an ester of orthosilicic acid. Thus Kipping (1,2) has employed the Grignard reagent and silicon tetrachloride to prepare the ethyl chloro silanes, while the alkyls of zinc and mercury have been employed by Friedel and Crafts (3).

Diethyl difluoro silane, T.2255 (II) is obtained in good yields by the fluorination of diethyl dichloro silane (XXI) either with antimony trifluoride, (Emeleus and Wilkins (4)) or ammonium fluoride (Wilkins (5)).

3. The alkyl alkoxy halo silanes represented by (XXII), have been grouped according to their specific alkoxy substituents

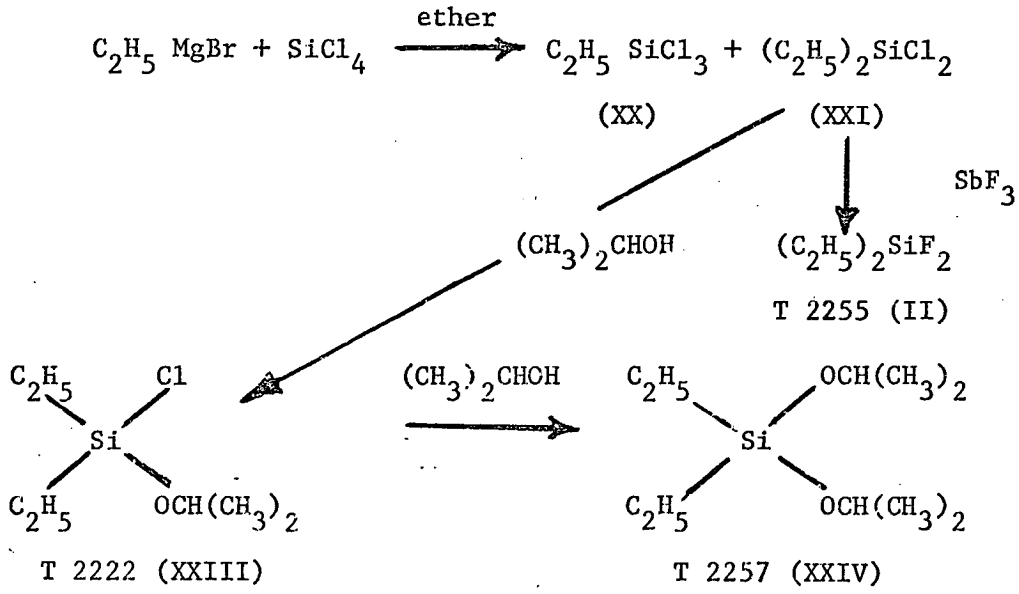


(XXII)

(a) The isopropyl esters

The silicon analogues of the "Sarins" (alkyl alkylfluoro-phosphinates) are obtained in formula (XXII) when n = 2, m = 1. Table II. B shows the structural relationship between isopropyl ethylfluorophosphinate, T.2109 (III) and isopropoxy diethyl fluoro silane, T.2256 (IV).

Depending on the amount of alcohol used, either the chloro alkoxy or the dialkoxy compound may be prepared from the dichloro silane. Thus McCusker and Greene (6) report a 72% yield of isopropoxy diethyl chloro silane, T.2222 (XXIII) from isopropanol and (XXI). Complete substitution by the alcohol gives diisopropoxy diethyl silane, T.2257 (XXIV). The equation of the reaction is:-

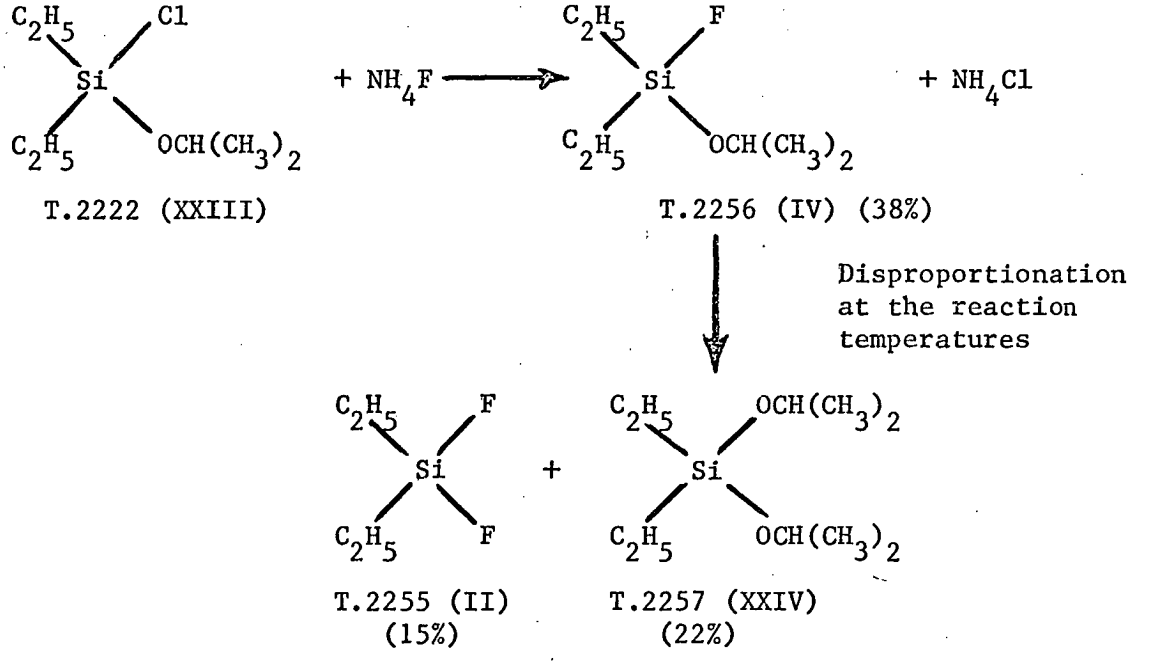


T 2222 (XXIII) T 2257 (XXIV)

The isopropyl esters of dimethyl dichloro silane can be prepared by an analogous method.

Considerable difficulty is experienced in fluorinating the alkoxy dialkyl chloro silanes. The fluorides of sodium and potassium are without action on the chloro body while stronger fluorinating agents split the ≡ Si - OR' bond. McCusker and Greene (6) report a yield of only 22% of isopropoxy diethyl fluoro silane, T.2256 (IV) from the fluorination of T.2222 (XXIII) with zinc fluoride. Antimony trifluoride (Booth and Carnell (7)), fluorosulphonic acid (Sowa (8)), and aqueous hydrofluoric acid (Marans, Sommer and Whitmore (9)) also split the ester groups from the alkoxy alkyl silanes to give good yields of the alkyl fluoro silanes.

Providing the reaction temperature is high enough, it has been found that ammonium fluoride will fluorinate the alkoxy dialkyl chloro silanes without difficulty. Thus isopropoxy diethyl fluoro silane, T.2256 (IV) is formed in a yield of 38% from T.2222 and ammonium fluoride. The presence of T.2255 (15%) and T.2257 (22%) in the reaction products suggests that a thermal disproportionation, at the temperature of the reaction, takes place according to the equation:-



T.2222 (XXIII)

T.2256 (IV) (38%)

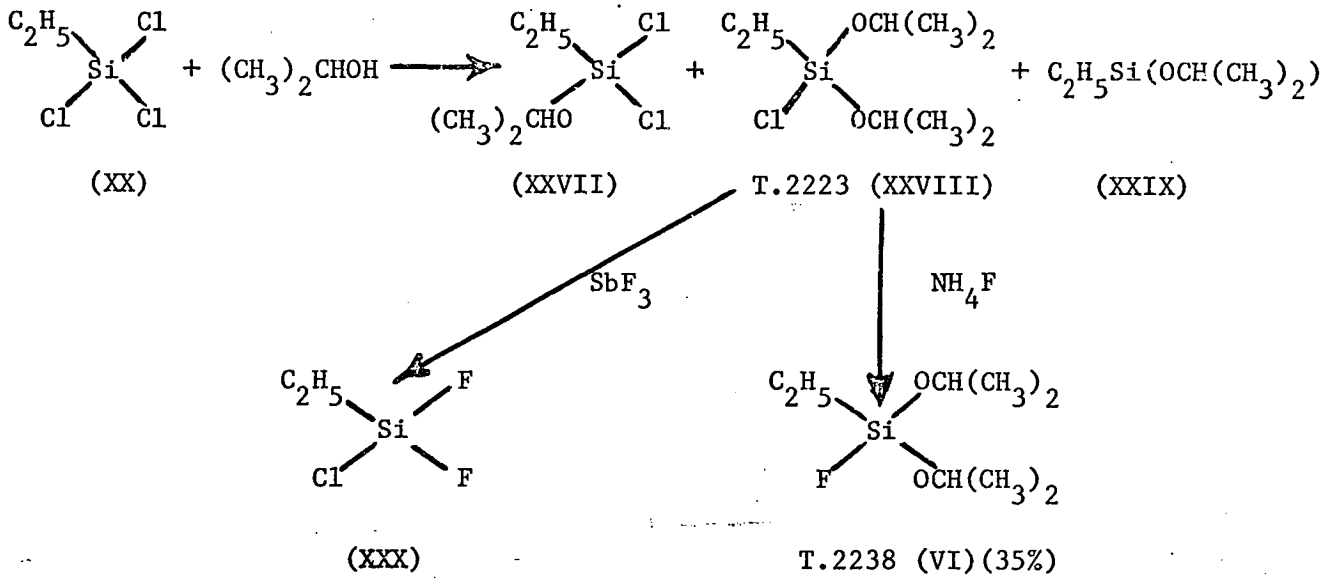
T.2255 (II) (15%)

T.2257 (XXIV) (22%)

Confirming the work of McCusker and Greene (6) it was not possible to fluorinate isopropoxy dimethyl chloro silane using the fluorides of zinc and antimony. Ammonium fluoride exhibits no reaction with this silane, either under reflux or under pressure in a heated sealed tube. Attempts to prepare isopropoxy dimethyl fluoro silane by the removal of an alkoxy group from diisopropoxy dimethyl silane were unsuccessful.

Organo-silanes, structurally related to the dialkyl fluoro phosphonates (Table II (C.) are obtained when n = 1, m = 2 in formula (XXII). Variation of the reaction conditions in the method of McCusker and Greene (6) gives either the mono, di or tri ester of the alkyl silanes. Isopropoxy ethyl dichloro silane (XXVII), diisopropoxy

ethyl chloro silane T.2223 (XXVIII) and triisopropoxy ethyl silane (XXIX) have all been obtained by this method.



Fluorination of T.2223 (XXVIII) with antimony trifluoride splits both ester linkages to form ethyl difluoro chloro silane (XXX). As in the case of T.2256(IV), ammonium fluoride will fluorinate T.2223 (XXVIII) to give diisopropoxy ethyl fluoro silane, T.2238(VI). Both T.2256 and T.2238 are colourless sweet-smelling liquids, soluble in common organic solvents, but insoluble in water.

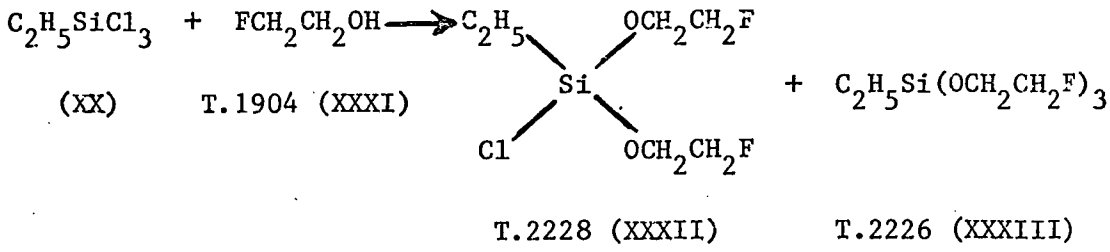
(b) The cyclohexyl esters

Cyclohexanol reacts readily with the alkyl chloro silanes, although the rate of reaction is slower than in the case of isopropanol. Ethyl trichloro silane (XX) with two moles of cyclohexanol gives dicyclohexyloxy ethyl chloro silane, T.2224 in good yields. Fractionation of cyclohexyloxy diethyl chloro silane, T.2225 prepared from (XXI), after it had been stored in a glass-stoppered bottle for six months, resulted in only a 50% recovery of pure compound.

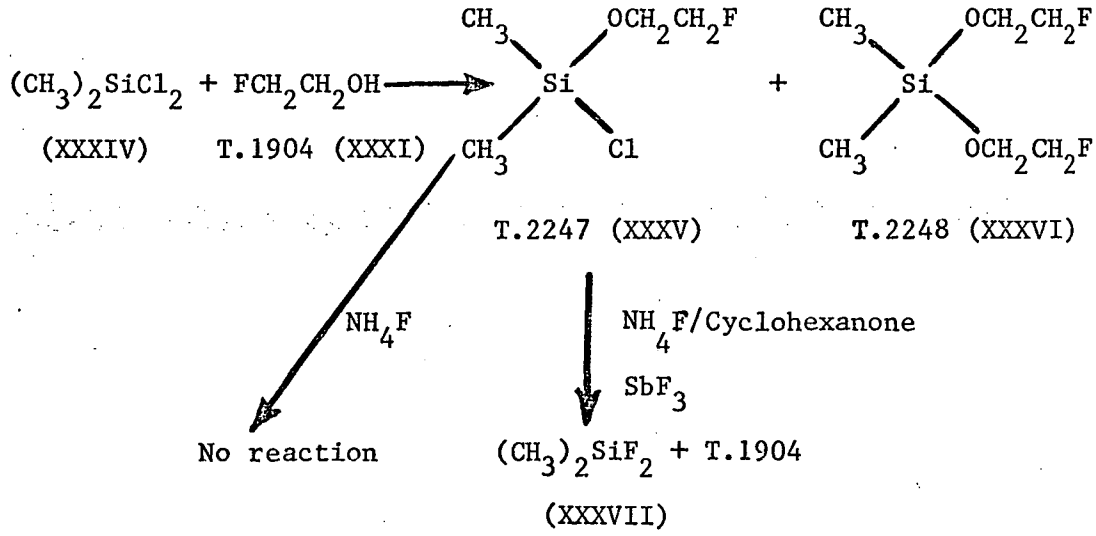
(c) The 2-fluoroethyl esters

The physiological assessment of those compounds designated so far by a T number indicated that they were all relatively non-toxic. The synthesis of a series of 2-fluoroethyl esters would, it was hoped, increase the toxicity of the substituted silane to a measurable value (10, 11 - p. 15). The toxicity of 2-fluoroethanol, T.1904 (XXXI) is 8 mg/Kg (LD50, mice, subcut).

Fractionation of the reaction mixture obtained from T.1904 (XXXI) and (XX) gives two compounds, namely bis(2-fluoroethoxy) ethyl chloro silane, T.2228 (XXXII) and tris(2-fluoroethoxy) ethyl silane, T.2226 (XXXIII).



In its reactions with the alkyl chloro silanes, T.1904 resembles cyclohexanol in being much less reactive than isopropanol. T.1904 (XXXI) reacts with dimethyl dichloro silane (XXXIV) to give the mono and di- 2-fluoroethoxy compounds. 2-Fluoroethoxy dimethyl chloro silane, T.2247 (XXXV) is a colourless fuming liquid readily hydrolysed by water, while bis(2-fluoroethoxy) dimethyl silane, T.2248 (XXXVI) is insoluble in water and non-reactive.



For toxicological requirements two homologues of T.2247 and T.2248 were prepared, namely 2-fluoroethoxy diethyl chloro silane, T.2229 and bis(2-fluoroethoxy) diethyl silane, T.2236.

The FCH_2CH_2O- group in the organo-silicon molecule appears to stabilize the Si-X bond, and all attempts to fluorinate T.2247 were unsuccessful. Although Wilkins (5) has reported a 90% yield of T.2255 on the fluorination of (XXI), b.p. 128°, with ammonium fluoride, T.2247, b.p. 126°, is not affected by refluxing with this fluorinating agent. When the solvent cyclohexanone, b.p. 155°, is used to increase the reaction temperature of the fluorination, ammonium fluoride splits the ester linkage to give a 75% recovery of 2-fluoroethanol.

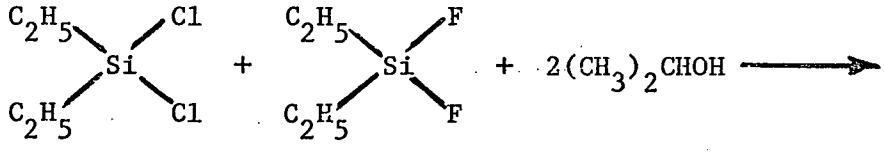
The fluorides of sodium and potassium are without action on T.2247, while zinc fluoride and antimony trifluoride react vigorously to split off the alcohol group and give dimethyl difluoro silane (XXXVII).

(d) The "di-di" reaction with organo-silanes

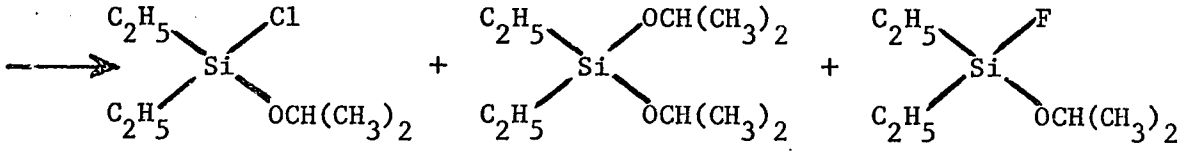
It has been known for some time, that the alkyl alkylfluoro-phosphinates may be prepared, in good yields, by means of the "di-di" reaction (12). Attempts to prepare the alkyl alkoxy fluoro silanes by a modification of this reaction has failed to give pure compounds. The "di-di" reaction, as postulated for the alkyl halo silanes, is represented by the equation:

$$R_2SiCl_2 + R_2SiF_2 + 2R'OH \longrightarrow 2R_2Si(F)OR' + 2HCl$$

When applied to diethyl dichloro silane (XXI), diethyl difluoro silane, T.2255 (II) and isopropanol however, side reactions occur resulting in a yield of only 15% of impure T.2256. The alcohol appears to react preferentially with the chloro silane to form the mono- and di- isopropoxy diethyl silanes, according to the equation,



(XXI) T.2255 (II)



T.2222 (XXIII) (21%) T.2257 (XXIV) (36%) T.2256 (IV) (15% impure)

This reaction is not unexpected since the alkyl fluoro silanes are much less reactive than the corresponding chloro compounds. McCusker and Greene (6) observed no reaction between isopropanol and T.2255 (II). The addition of an equimolar quantity of sodium to the reaction mixture however, gave a 25% yield of T.2256 (IV). On the other hand Eaborn (13) could not isolate ethoxy diisopropyl fluoro silane from the reaction between diisopropyl difluorosilane, ethanol and sodium but recovered unchanged starting material and diethoxy diisopropyl silane.

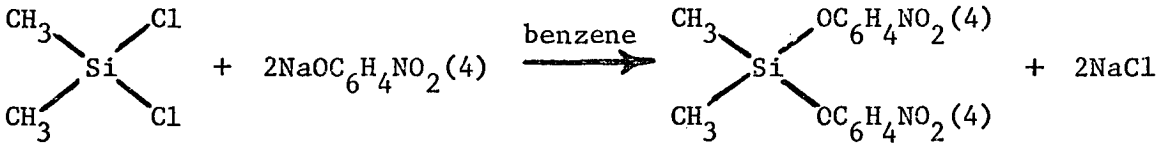
It appears that the failure of the "di-di" reaction with silicon dihalides, as compared to phosphonyl dihalides, is due to the stability of the dialkyl difluoro silanes, towards the alcohols. The low boiling point of dimethyl difluoro silane (XXXVII), (b.p. +3°), limits its use in any possible "di-di" reaction.

4. Replacement of an ethyl group in non-toxic triethyl phosphate by p-nitro phenyl, gives the insecticide "Paraoxon", T.2220 (diethyl, p-nitro phenyl phosphate), which has an unexpectedly high toxicity towards warm-blooded animals. Attempts to prepare some p-nitro phenoxy substituted silanes has given the alkyl aryloxy silanes (XXXVIII).

$$RnSi(OPh)4 - n$$

(XXXVIII)

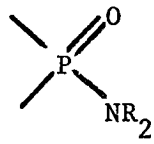
p-Nitro phenol itself will not react with the alkyl chloro silanes under the same conditions as applied for the aliphatic alcohols. Frost (14) has recently reported that the use of triethylamine as an acid acceptor in the preparation of substituted silanes is not advisable, since tertiary amines form stable complexes with silicon halides. Dry sodium p-nitro phenate and alkyl chloro silanes react together in dry benzene to form the completely substituted silicon compound. The reaction with (XXXIV) is:



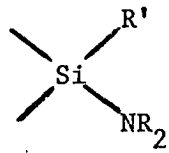
(XXXIV) T.2245 (XXXIX)

Bis(p-nitro phenoxy) dimethyl silane, T.2245 (XXXIX) and tris(p-nitro phenoxy) ethyl silane, T.2227 prepared by the above method are light coloured, non-distillable solids, that are difficult to crystallize. They are both readily hydrolysed by water with the liberation of p-nitro phenol. The toxicities (rats, subcut.) of T.2227 and T.2245 are very similar to the toxicity of p-nitro phenol, T.2246, itself.

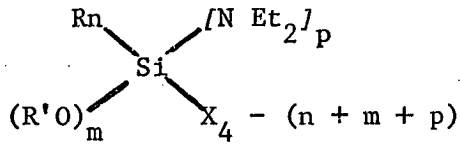
5. (a) Since many toxic phosphorus compounds contain the



group, a series of organo-silicon compounds with the



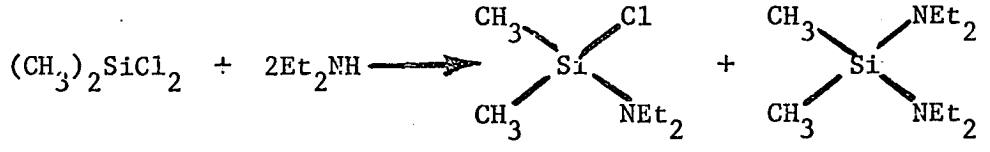
group, has been prepared. In all cases the diethylamino group has been used, and the general formula of the alkoxy diethylamino alkyl halo silanes can be represented by (XL)



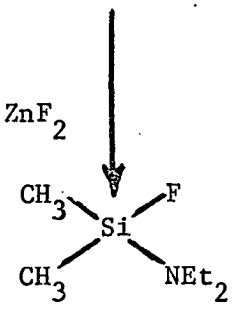
(XL)

(b) The structural analogues of the alkyl dialkylamidofluorophosphine oxides are obtained when n = 2, m = 0, p = 1 in formula (XL), Table II. D). The dialkylamino alkyl halo silanes have not been reported, although Larsson and Smith (15) and Anderson (16) have both described the bis(mono- and dialkylamino) dialkyl silanes. Neither Anderson (16) nor Johannson (17) were able to obtain bis(diethylamino) dimethyl silane, T.2241 (XLII), in a

pure state. The reaction of two moles of diethylamine to each mole of dimethyl dichloro silane (XXXIV) gives diethylamino dimethyl chloro silane, (XLI) in good yields. T.2241 (XLII) is formed as a byproduct.



(XXXIV) (XLI) T.2241 (XLII)

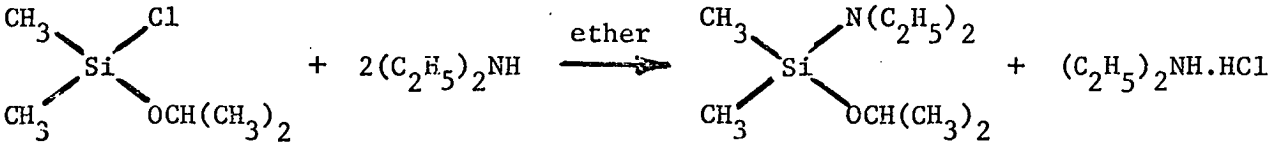


T.2249 (VIII)

Diethylamino dimethyl chloro silane (XLI) is an extremely reactive colourless fuming liquid. It hydrolyses with great rapidity with the liberation of diethylamine hydrochloride. T.2241 on the other hand, is unreactive and very slowly hydrolysed by water. Those silanes with a chlorine and a diethylamino group together on the same silicon atom are extremely reactive and difficult to handle. Replacement of the chlorine by a fluorine, alkoxy, or further dialkylamino group, markedly reduces the activity of the silane.

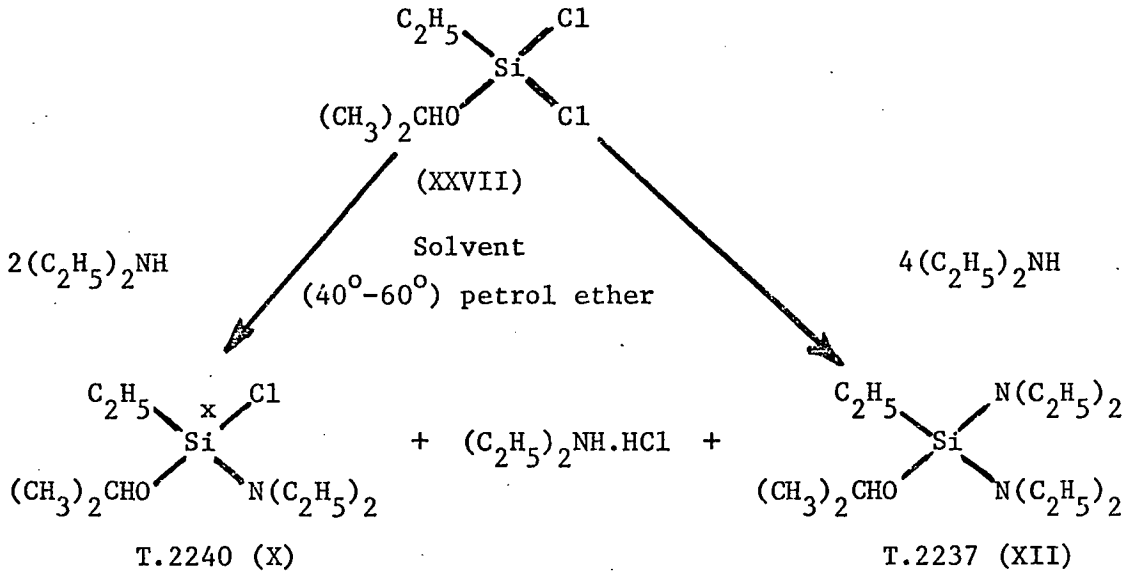
Compound (XLI) can be fluorinated with zinc fluoride to give diethylamino dimethyl fluoro silane, T.2249 (VIII) in poor yield. Ammonium fluoride is unsuitable since it breaks the Si - N bond.

(c) The <u>alkoxy dialkylamino dialkyl silanes</u> (n = 2, m = 1, p = 1 in (XL)) are obtained in good yields when diethylamine is added to a stirred solution of an alkoxy dialkyl chloro silane in ether. Isopropoxy diethylamino dimethyl silane, T.2239 (XLV) prepared by this method is a stable colourless liquid, immiscible with water but soluble in organic solvents.



(XLIV) T.2239 (XLV)

(d) The alkyl alkoxy dichloro silanes react with diethylamine to form two different compounds. With (XXVII) the reaction is:-

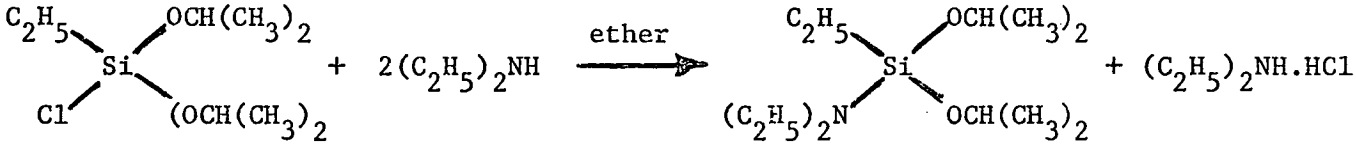


T.2240 (X) T.2237 (XII)

Isopropoxy diethylamino ethyl chloro silane, T.2240 is a colourless, reactive, fuming liquid. It contains an asymmetric silicon atom, and is structurally similar to the weak insecticide isopropyl dimethylamidochlorophosphinate (IX) (Table II. E) that has been reported by Schrader (11 - p. 79).

Isopropoxy bis(diethylamino) ethyl silane, T.2237 (XII) is much less reactive than its related compound T.2240, and thus resembles compound T.2241. Michaelis (18) has reported the non-toxic compound ethyl bis(diethylamido) phosphinate (XI) the structure of which may be arbitrarily compared to that of T.2237 as shown in Table II (F).

(e) When n = 1, m = 2, p = 1 in formula (XL) a new series of dialkoxy diethylamino alkyl silanes is formed. Diethylamine reacts with T.2223 (XXVIII) to form diisopropoxy diethylamino ethyl silane, T.2235 (XIV).



T.2223 (XXVIII) T.2235 (XIV)

Table II (G) shows the structure of diethyl diethylamido-phosphonite (XIII) as reported by Michaelis (18). T.2235 (XIV), a colourless and stable liquid is structurally similar to the organo-phosphorus compound (XIII).

(f) A different type of nitrogen-containing silane is obtained when m = 3, p = 1 in formula (XL). The alkoxy dialkyl amino silanes which have no direct C - Si bond, have been described by Joffe and Post (19) and by Rosnati (20). Application of their synthetic methods according to the equation:-

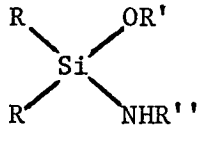
$$(C_2H_5O)_3SiCl + 2(C_2H_5)_2NH \longrightarrow (C_2H_5O)_3Si\,N(C_2H_5)_2 + (C_2H_5)_2NH.HCl$$

(XLIX) T.2252 (L)

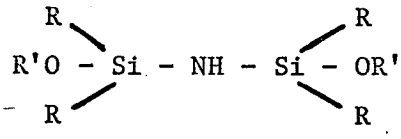
has given triethoxy diethylamino silane, T.2252 (L). Schumb and Stevens (21) have described the preparation of triethoxy chloro silane (XLIX) by the partial alcoholysis of $SiCl_4$ in ether.

T.2252 (L) is much less stable than T.2235 (XIV) and although it contains no halogen group it appears to resemble T.2240 (X). This presumably is due to the absence of any stable C - Si bonds.

6. The alkoxy monoalkylamino dialkyl silanes represented by the general formula (LI), are closely allied structurally to the alkoxy dialkylamino alkyl silanes (XL) and the symmetrical dialkoxy tetra-alkyl disilazanes (LII).

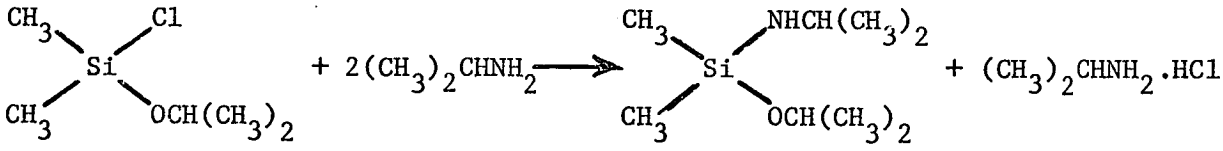


(LI)



(LII)

Application of the method of Kraus and Nelson (22) according to the equation:-

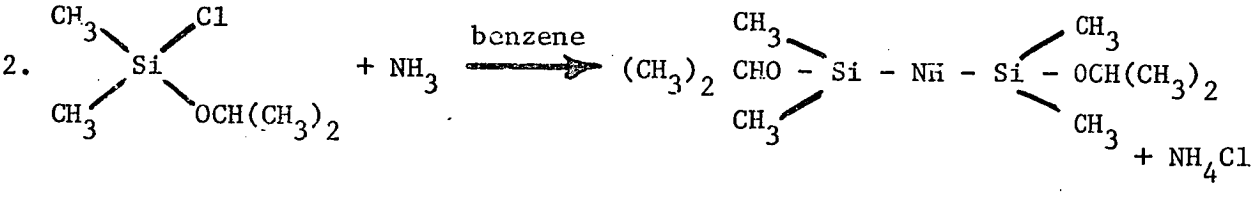


(XLIV) T.2254 (LIII)

gives isopropoxy isopropylamino dimethyl silane, T.2254 (LIII), from the reaction of (XLIV) and isopropylamine. Although Sauer (23) reports that the free amino hydrogen of the monoalkylamino alkyl silanes can be further substituted, no disilazane (LII) was obtained during the preparation of T.2254 (LIII).

In its chemical reactions, T.2254 resembles the alkoxy dialkylamino alkyl chloro silane, T.2240.

7. The alkyl alkoxy disilazanes (LII), characterized by the Si-N-Si grouping, are closely allied structurally to the disiloxanes. Modification of the method of Rosnati (20) for the synthesis of aryl alkoxy disilazanes,

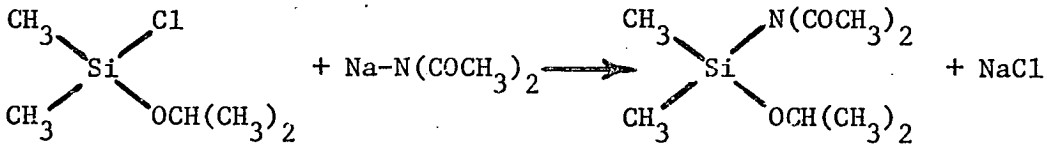


(XLIV) T.2258 (LIV)

gives symmetrical diisopropoxy tetramethyl disilazane, T.2258 (LIV) in good yields.

In comparison to the Si-N bond, the Si-N-Si bond is very stable, being unattacked by boiling water or dilute alkali. It is, however, split quantitatively by dilute mineral acids.

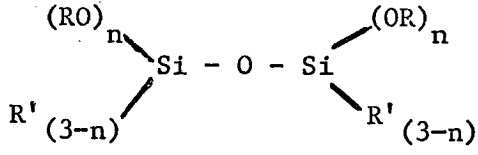
8. Replacement of the amino alkyl groups in the alkoxy dialkylamino dialkyl silanes with acetyl groups, gives the alkoxy diacetylamino dialkyl silanes. Diacetimide itself will not react with the alkoxy alkyl chloro silanes, and as in the case of the alkyl aryloxy silanes, the use of a tertiary base to promote the reaction is not advisable. Sodium diacetimide (LV) in toluene, however, reacts with (XLIV) to give isopropoxy diacetylamino dimethyl silane, T.2244 (LVI) in good yields.



(XLIV) (LV) T.2244 (LVI)

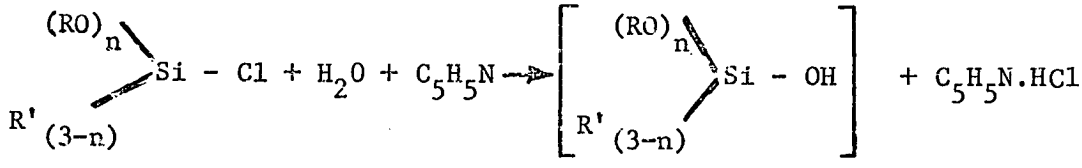
Structurally and chemically, T.2244 is similar to the diethylamino-substituted silane, T.2239 (XLV). Both compounds are colourless, unreactive liquids, insoluble in water, and each exhibits the strong odour of the amine substituent.

9. In the organo-phosphorus field, the pyrophosphonates resemble the "Sarins" both chemically and toxicologically. Symmetrical silicon compounds of comparable structure to the pyrophosphonates are the alkyl alkoxy disiloxanes, represented by (LVII).

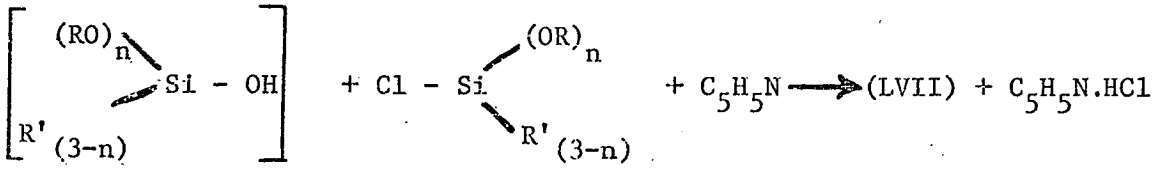


(LVII)

Peppard, Brown and Johnson (24) have prepared various alkoxy disiloxanes (alkyl disilicates) from the alkoxy chloro silanes, water and pyridine. Alkyl alkoxy chloro silanes undergo a similar reaction to give the corresponding disiloxanes. The controlled hydrolysis of the chloro silane liberates unstable alkyl alkoxy silanol (LVIII), which then condenses with the unchanged chloro body to give the required disiloxane.



Note. R, R' ≤ 3C. (LVIII) (unstable)



(LVII)

Ford-Moore (25) has shown that the pyrophosphonates may be prepared by an analogous method.

Symmetrical diisopropoxy tetramethyl disiloxane, T.2251 (XVI), prepared by the above method from (XLIV) is structurally similar to diisopropyl dimethyl pyrophosphonate, T.2121 (XV) in the phosphorus series, Table II, H. The disiloxanes resemble the disilicates and the disilazanes in being colourless, chemically inactive compounds. They are immiscible with water in all proportions, but soluble in common organic solvents. Replacement of the Si-O-Si group in T.2251 by the Si-NH-Si group gives the disilazane, T.2258 (LIV).

It is interesting to note that strong alkalis cleave the ester linkages of the alkyl alkoxy chloro silanes to form alkyl cyclosiloxanes.

$$R_2Si(OR')Cl + R'OH + KOH \longrightarrow [R_2SiO]_3 + [R_2SiO]_4 \quad \text{etc.}$$

The preparation of cyclotri- and cyclotetrasiloxanes from isopropoxy dimethyl chloro silane (XLIV), isopropanol and potassium hydroxide has been described by McCusker and Greene (6).

The strong insecticidal activity of tetraethyl pyrophosphate, TEPP, T.2140 (XVII), suggested the preparation of sym. tetraisopropoxy diethyl disiloxane T.2253 (XVIII) (by the controlled hydrolysis of T.2223)

$$2\ (CH_3)_2CHO\,C_2H_5\,Si\,(CHO)_2CH_3 - Cl + H_2O + C_5H_5N \longrightarrow C_2H_5 - Si(CHO)_2CH_3 - O - Si(OCH(CH_3)_2)_2 - C_2H_5$$

T.2223 (XXVIII) T.2253 (XVIII)

Although T.2253 (XVIII) can be structurally compared with TEPP (XVII) (Table II, I), the latter compound has no C-P bonds while two C-Si bonds are present in T.2253.

Hexaethoxy disiloxane T.2250 was therefore prepared from triethoxy chloro silane, (XLIX) by the method of Peppard, Brown and Johnson (24). It is chemically similar to T.2251 (XVI) and T.2253 (XVIII). All the disiloxanes so far prepared have been found to be physiologically inactive.

10. Attempts to substitute the chlorine group of the alkyl alkoxy chloro silanes by a cyano group were unsuccessful. The cyanides of sodium, potassium, copper and silver are all unreactive and this agreed with work on some alkyl cyano silanes as reported by Eaborn (26).

11. An infra-red trace of all the silicon compounds mentioned has been obtained, and these results will be reported later.

Toxicology

Although many organo-silicon compounds have been reported, few have been found to be physiologically active. Wolinski, Tieckelmann and Post (27) report that the trialkyl mercapto silanes have some toxic properties, while Speier (28) has recently shown that the hydroxy methyl trialkyl silanes are valuable antiseptics. Several of the silicon analogues of the "nerve gases" have been toxicologically assayed by McCusker and Greene (6), but re-evaluation of the toxicities of the same compounds has given figures that do not agree with the reported results.

The toxicities of the silanes were determined by the subcutaneous route in mice or rats, and the intravenous route in rabbits. No attempt has been made to calculate the precise LD50 values, since the small number of animals contributing to any individual evaluation would impose wide confidence limits on the results obtained. The results with rabbits by the intravenous route generally agree with the values obtained using subcutaneously injected mice, although the LD50 estimations of the former are less reliable. With very high intravenous doses of the less toxic silanes, death occurred in rabbits due to pulmonary fatty emboli and could not be attributed to an intrinsic toxicity of the silicon molecule itself.

The series of compounds tested fall naturally into several groups. One group containing the 2-fluoroethoxy substituent, and including 2-fluoroethanol itself, has toxicities in the range 8-25 mg/kg, while the majority of the silanes are comparatively non-toxic, the LD50 being considerably greater than 800 mg/kg. Intermediate is the group of p-nitro phenoxy substituted silanes, T.2255 and T.2249 with LD50 values around 600 mg/kg. Table III gives the approximate values or the maximal or minimal indications for the LD50's of the relatively non-toxic silanes, while Table IV shows the toxicological results for the 2-fluoroethoxy substituted compounds. The toxicity values for the p-nitro phenoxy derivatives are listed in Table V.

Although many of the organo-silanes tested have structures simulating some of the most toxic phosphorus compounds known, the silicon molecule itself appears to possess little, if any, intrinsic toxicity. The alkyl chloro and fluoro silanes, together with their isopropyl and cyclohexyl esters are all comparatively non-toxic. Thus replacement of the (P=O) group in T.2109 by the ($Si-C_2H_5$) group reduces the LD50 value of the former from 0.125 mg/kg (rats, subcut.) to a value greater than 800 mg/kg. (mice, subcut.) for the silane T.2256. Similarly the "DEP-type" silane, T.2238 has an LD50 value greater than 800 mg/kg (mice, subcut.).

All the dialkylamino substituted silanes are relatively non-toxic, although T.2249, the silicon analogue of the toxic methyl dimethylamido-fluorophosphine oxide, T.2211 has an LD50 around 600 mg/kg (mice, subcut.). The chemical reactivity of the dialkylamino silanes does not appear to affect their physiological activity. Thus the stable bis(diethylamino) dimethyl silane, T.2241 and the very reactive silane T.2240 containing an asymmetric silicon atom, are both non-toxic. Similarly variation in the number of alkyl, alkoxy or dialkylamino groups does not measurably enhance the toxicity of the compound as shown by the LD50 values of T.2235, T.2237, T.2239 and T.2240 in Table III.

The absence of all stable carbon-silicon bonds in T.2252, or the presence of an active amino hydrogen in T.2254, also does not contribute

any toxic properties to the silicon molecule. As shown by the toxicological data of T.2258 in Table III, the Si-N-Si bond can be grouped with the Si-N bond as being physiologically inactive. Replacement of the amino-alkyl groups of T.2239 by acetyl groups, to give T.2244, does not increase the LD50 value of the former by any measurable amount.

Although the disiloxanes resemble the pyrophosphonates both in structure and chemical reactivity, they have quite dissimilar physiological properties. The LD50 value of diisopropyl dimethyl pyrophosphonate, T.2121 is 0.12 mg/kg (rats, subcut.) (25), but its silicon analogue T.2251 (Table II, H) is ineffective against mice (subcut.) at doses up to 800 mg/kg. Similarly, although TEPP, T.2140 is a powerful systemic insecticide the analogous disiloxane, T.2253 (Table II, I) is non-toxic to warm-blooded animals.

Hexaethoxy disiloxane, T.2250 resembles the other disiloxanes in being physiologically inactive and when assayed for possible insecticidal activity it was found to be ineffective against mosquitos (Aedes aegypti). Also no deaths were recorded among houseflies (Musca domestica) when they were exposed to a solution of T.2250 in liquid paraffin. In both these insecticidal tests the conditions of the experiment were such as to correspond at least to the Median Lethal Concentration value for DDT. The insolubility of the disiloxanes in water precluded any attempts at evaluating their possible toxicity against Gammarus pulex.

The introduction of a toxic group onto the silicon atom appears to impart the toxic properties of that group to the newly-formed silane. Schrader (11 - p.15) has already shown that sulphites, sulphoxides, urethanes and acetals derived from 2-fluoroethanol have powerful insecticidal properties and it is not unexpected therefore that the 2-fluoroethoxy substituted silanes should also show toxic action. Replacement of the isopropyl group of T.2222 by the 2-fluoroethyl group gives T.2229 with over a sixtyfold increase in the LD50 value of the former compound. In the phosphorus series, however, replacement of the isopropyl methylfluorophosphinate, T.2106 by the 2-fluoroethyl group gives T.2154 having an LD50 three times less than that of T.2106.

In the six 2-fluoroethoxy substituted silanes prepared, variations were made in the number of alkyl and 2-fluoroethoxy groups. Although the LD50's of the compounds vary between 8-25 mg/kg (mice, subcut.) and the R.M.T. (T.1904 = 100) between 90 and 250, the R.M.T. per mole of 2-fluoroethanol in the molecule is remarkably constant. The probability that the toxicity of the silanes is mainly due to 2-fluoroethanol receives considerable support from these figures. The physiological symptoms obtained on the subcutaneous injection of these silanes into mice are practically identical to those found with 2-fluoroethanol itself. Thus, although the compounds produce lethargic effects resembling partial to almost complete anaesthesia, followed by death, post-mortem reveals no gross abnormalities. The time of onset of symptoms for T.1904 and the 2-fluoroethoxy alkyl chloro silanes, T.2228, T.2229 and T.2247 is less than that for the more stable silanes T.2226, T.2236 and T.2248. This is not inconsistent with the theory that the toxicity of these compounds is due entirely to the 2-fluoroethanol, liberated by hydrolysis into the blood stream.

The p-nitro phenyl esters confirm the results obtained with the 2-fluoroethyl esters. Although the R.M.T.'s for T.2227 and T.2245 are approximately twice the R.M.T. value of p-nitro phenol, T.2246 itself, the R.M.T.'s per mole of p-nitro phenol, for the three compounds are in good agreement. Again the physiological symptoms of T.2227 and T.2245 are identical with those obtained using T.2246 alone, indicating that the toxic nature of these silanes is due entirely to the p-nitro phenol liberated by hydrolysis.

From these results the following conclusions may be drawn:

(a) Replacement of the (P=O) group in the toxic organo-phosphorus compounds by the (Si-R) group, markedly reduces the toxicity of the former compounds.

(b) While the silicon molecule itself appears to possess no intrinsic toxicity the introduction of a toxic substituent imparts its toxic properties to the molecule as a whole.

(c) The low toxicity of the few silicon analogues of the organo-phosphorus compounds prepared and tested, does not give great hope for finding highly active compounds in this field.

Acknowledgements

The toxicological assessments were made by W/Cmdr. A. Muir, R.A.F., S. Callaway and F. Burgess. F.E. Charlton and Miss B.A. Jones carried out the carbon, hydrogen and chlorine determinations. The insecticidal tests were made by the Colonial Insecticide Research Unit, Porton.

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PD/JY.

TABLE I

List of T numbers, etc.

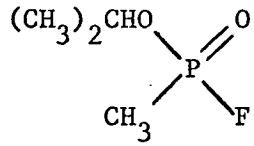
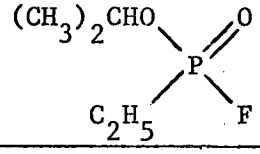
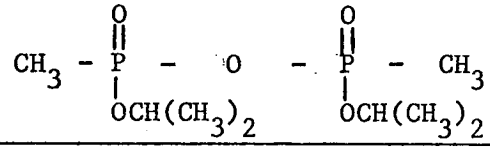
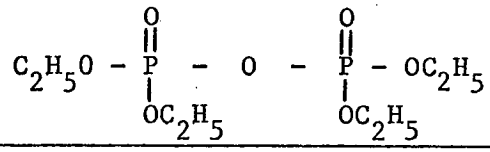
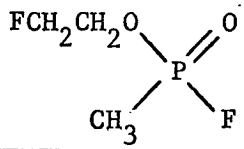
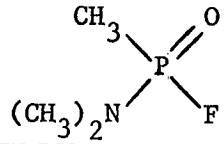
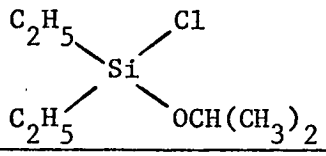
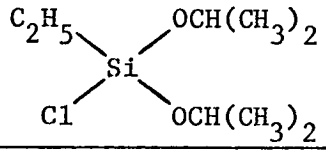
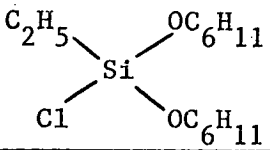
Compound	Formula	T number
2- Fluoroethanol	FCH_2CH_2OH	T.1904
Isopropyl methylfluoro-phosphinate		T.2106
Isopropyl ethylfluoro-phosphinate		T.2109
Diisopropyl dimethyl pyrophosphonate		T.2121
Tetra ethyl pyrophosphate		T.2140
2-Fluoroethyl methyl-fluorophosphinate		T.2154
Methyl dimethylamido-fluorophosphine oxide		T.2211
Isopropoxy diethyl chloro silane		T.2222
Diisopropoxy ethyl chloro silane		T.2223
Dicyclohexyloxy ethyl chloro silane		T.2224

TABLE I (Cont'd.)

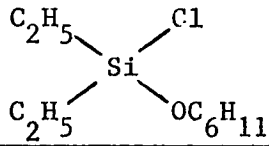
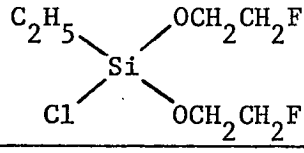
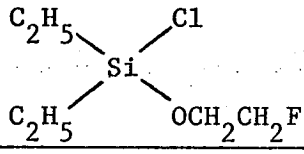
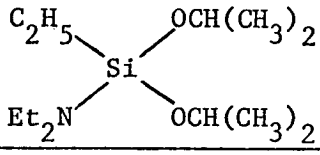
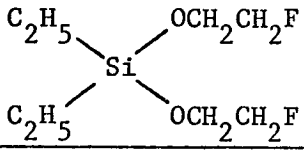
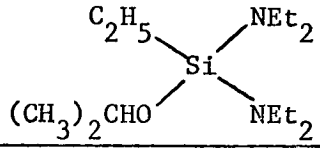
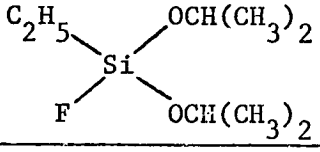
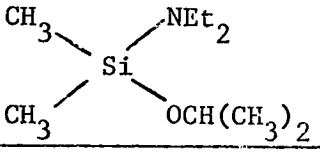
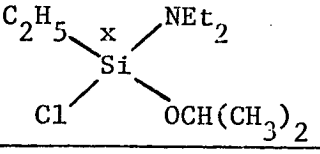
Compound	Formula	T number
Cyclohexyloxy diethyl chloro silane		T.2225
Tris(2-fluoroethoxy) ethyl silane	$C_2H_5Si(OCH_2CH_2F)_3$	T.2226
Tris(p-nitro phenoxy) ethyl silane	$C_2H_5Si(OC_6H_4NO_2(4))_3$	T.2227
Bis(2-fluoroethoxy) ethyl chloro silane		T.2228
2-Fluoroethoxy diethyl chloro silane		T.2229
Diisopropoxy diethylamino ethyl silane		T.2235
Bis(2-fluoroethoxy) diethyl silane		T.2236
Isopropoxy bis(diethyl-amino) ethyl silane		T.2237
Diisopropoxy ethyl fluoro silane		T.2238
Isopropoxy diethylamino dimethyl silane		T.2239
Isopropoxy diethylamino ethyl chloro silane		T.2240

TABLE I (Cont'd.)

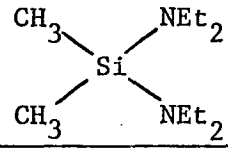
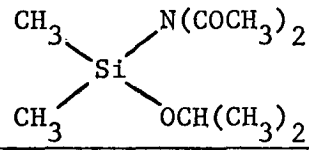
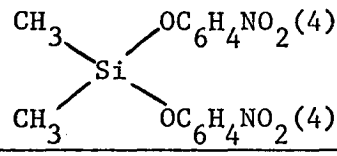
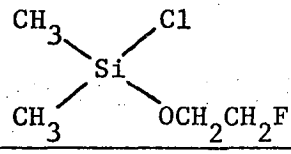
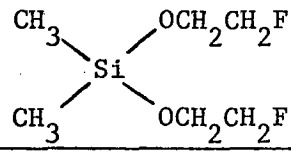
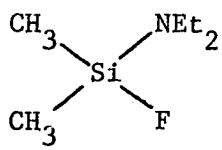
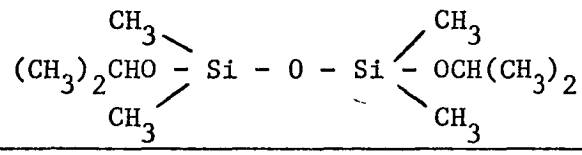
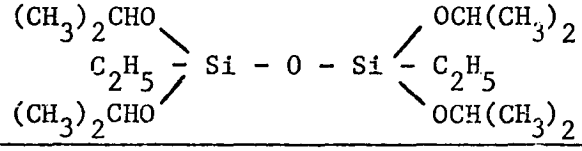
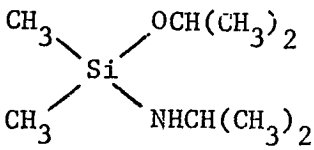
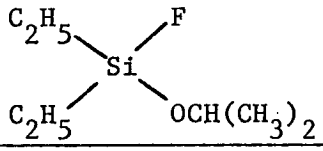
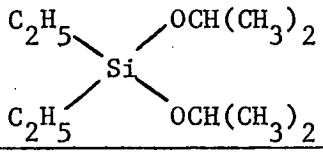
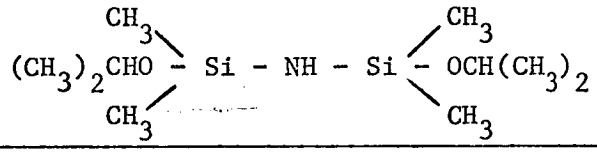
Compound	Formula	T number
Bis(diethylamino) dimethyl silane		T.2241
Isopropoxy diacetylamino dimethyl silane		T.2244
Bis(p-nitro phenoxy) dimethyl silane		T.2245
p-Nitro phenol	$HOC_6H_4NO_2(4)$	T.2246
2-Fluoroethoxy dimethyl chloro silane		T.2247
Bis(2-fluoroethoxy) dimethyl silane		T.2248
Diethylamino dimethyl fluoro silane		T.2249
Hexaethoxy disiloxane	$(C_2H_5O)_3Si - O - Si(OC_2H_5)_3$	T.2250
Sym. diisopropoxy tetra methyl disiloxane		T.2251
Triethoxy diethylamino silane	$(C_2H_5O)_3SiNEt_2$	T.2252
Sym. tetra isopropoxy diethyl disiloxane		T.2253
Isopropoxy iso-propylamino dimethyl silane		T.2254

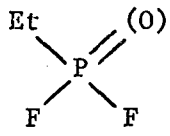
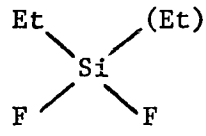
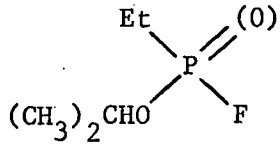
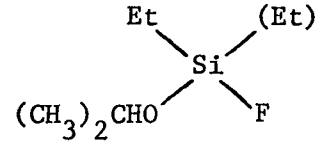
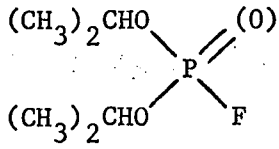
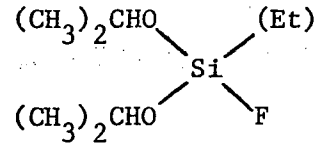
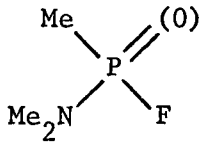
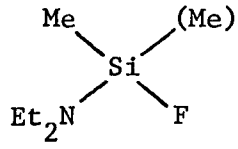
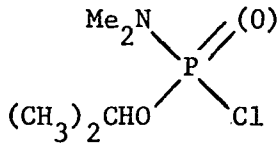
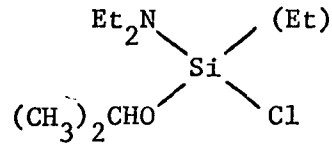
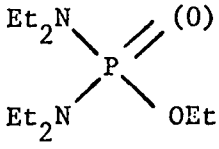
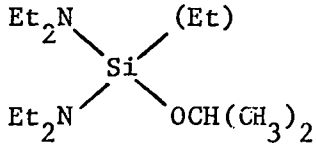
TABLE I (Cont'd.)

Compound	Formula	T number
Diethyl difluoro silane	$(C_2H_5)_2SiF_2$	T.2255
Isopropoxy diethyl fluoro silane		T.2256
Diisopropoxy diethyl silane		T.2257
Sym. diisopropoxy tetramethyl disilazane		T.2258

x Asymmetric silicon atom.

TABLE II

Comparative structure of phosphorus and silicon compounds

(A)	 (I)	 T 2255 (II)
(B)	 T 2109 (III)	 T 2256 (IV)
(C)	 DFP (V)	 T 2238 (VI)
(D)	 T 2211 (VII)	 T 2249 (VIII)
(E)	 (IX)	 T 2240 (X)
(F)	 (XI)	 T 2237 (XII)

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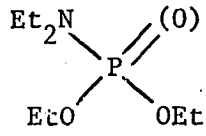
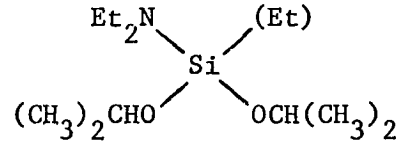
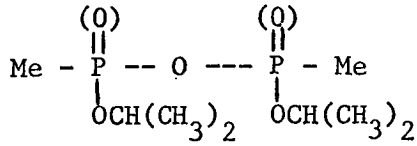
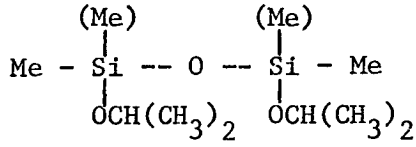
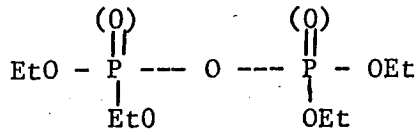
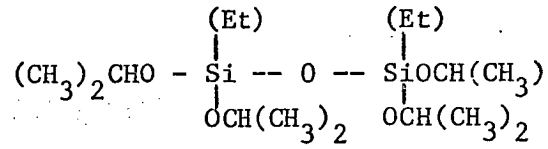
(G)	 (XIII)	 T 2235 (XIV)
(H)	 T 2121 (XV)	 T 2251 (XVI)
(I)	 T 2140 (XVII) TEPP	 T 2253 (XVIII)

TABLE III

Approximate LD50's of relatively non-toxic silanes

T Number	LD50 (mg/kg)	
	Mice Subcut.	Rabbits I.V.
2222	>1600	>200
2223	> 800	>100
2224	> 800	>100
2225	-	>100
2235	> 800	> 50
2237	> 800	> 50
2238	> 800	-
2239	> 800	> 50
2240	> 800	> 50
2241	> 800	> 50
2244	> 800	> 50
2249	ca 600	> 50
2250	> 800	> 50
2251	> 800	> 50
2252	> 800	> 50
2253	> 800	> 50
2254	> 800	> 50
2255	> 800	> 50
2256	> 800	> 50
2257	> 800	> 50
2258	> 800	> 50

TABLE IV

LD50's and R.M.T.'s of 2-fluoroethoxy substituted silanes

T Number	LD50 (mg/kg)		R.M.T.	R.M.T. per mole of FCH_2CH_2OH
	Mice (subcut.)	Rabbits I.V.		
1904	8	<2.5	100	100
2226	12	<50	253	84
2228	15	<50	180	90
2229	25	< 5	91	91
2236	15	-	176	88
2247	13	-	150	150
2248	13	-	178	89

TABLE V

LD50's and R.M.T's of p-nitrophenoxy substituted silanes

T Number	LD50(mg/kg)	R.M.T.	R.M.T. per mole of $HOC_6H_4NO_2$(4)
	Rats (subcut.)		
2227	ca 800	210	70
2245	ca 600	200	100
2246	ca 500	100	100

APPENDIX I

Experimental Results

1. The alkyl halo silanes

(A) The preparation of diethyl dichloro silane illustrates the general method of preparing the ethyl chloro silanes by means of the Grignard reaction (Note 1).

Ethyl magnesium bromide was prepared in 91% yields (Note 2) from magnesium (78 g = 3.25 mole), ethyl bromide (354 g = 3.25 mole) and sodium-dried ether (750 ml) (Notes 3, 4). Silicon tetrachloride (220 g = 1.3 mole) (Note 5), in ether (1200 ml) (Note 6), was placed in a 3-litre flask, fitted with a dropping funnel and powerful electric stirrer. During the slow addition of the ethyl magnesium bromide (2.95 moles) over a period of two hours, the temperature of the reaction mixture was maintained at -15°. After standing overnight the supernatant liquid was decanted and the precipitated magnesium salts washed twice with ether. The ether was removed from the solution by distillation through an 18" Fenské column packed with glass helices, and the residue then fractionated to give the following products:

(i) Ethyl trichlorosilane, b.p. 98°. η_D^{25} 1.4239.
Yield 45 g (21%)

(ii) Diethyl dichlorosilane, b.p. 128° - 129°. η_D^{25} = 1.4292
Yield 100 g (49%)

(iii) Triethyl chlorosilane, b.p. 144°. η_D^{25} 1.4357.
Yield 15 g (8%)

Ethyl trichloro silane was formed in 60-70% yields in the above reaction, when the ratio C_2H_5 MgBr:$SiCl_4$ was 1:0.9.

Notes

(1) Although Karasch, Jensen and Weinhouse (29) could monoethylate the chlorides of phosphorus, arsenic and antimony with lead tetraethyl, attempts to prepare the ethyl chloro silanes by this method were unsuccessful.

(2) The "active" Grignard content of the solution was estimated by the method of Gilman, Wilkinson, Fishel and Meyers (30).

(3) Recently Adrianov (31) has reported that the replacement of ether in the Grignard reaction by benzene gave increased yields of product. Our experiments, however, failed to confirm this.

(4) No iodine should be used to initiate the Grignard reaction since its presence contaminates the final products.

(5) The silicon tetrachloride as supplied by Messrs. British Drug Houses Ltd., had b.p. 58°, η_D^{25} 1.4120.

(6) Reuse of the ether obtained from the final distillation of the silanes gave an increased yield of products.

(B) Technical dimethyl dichloro silane from Messrs. Midland Silicones Ltd., was refractionated through a 48" column packed with nickel Steadman rings. The product had b.p. 69.5° - 69.7°/753 mm, η_D^{25} 1.4025. Found: Cl 54.9. Calc. for $C_2H_6Cl_2Si$: Cl 54.9%.

(C) T.2255

This compound was prepared by the method of Wilkins (5) from diethyl dichloro silane and antimony trifluoride. It had b.p. 62°, η_D^{25} 1.3382. Yield 84%. Found: F 30.7, 30.9. Calc. for $C_4H_{10}F_2Si$: F 30.6%.

2. The alkyl alkoxy halo silanes

(A) Isopropoxy dimethyl chloro silane.

The preparation described below is the standard method for preparing the substituted silicon esters. Dimethyl dichloro silane (171 g = 1.33 moles) is placed in a three-necked flask fitted with a reflux condenser, protected by a calcium chloride tube, a dropping funnel and an efficient stirrer. With the contents of the flask gently refluxing anhydrous isopropanol (80g = 1.33 moles) is slowly added over a period of 2.5 hours. After the final addition of the alcohol the system is refluxed for a further two hours, or until the majority of the hydrogen chloride formed during the reaction has been removed.

Fractionation through an efficient column gives the product, b.p. 106.5°, η_D^{25} 1.3914. Yield 129 g (64%). Found: Cl 23.1. Calc. for $C_5H_{13}OClSi$: Cl 23.2%. Diisopropyl dimethyl silane, b.p. 132°, η_D^{25} 1.3842 is also obtained from the reaction mixture. The yield is 20 g (9%). Found: C 54.3 H 11.0. Calc. for $C_8H_{20}O_2Si$: C 54.5 H 11.4%.

(B) The isopropoxy and cyclohexyloxy esters of the ethyl silanes were prepared in a manner analogous to that given above. The results of these experiments are summarized in Table VI.

Notes

(7) Benzene was used as a solvent in order to prevent overheating of the reaction mixture.

(8) The addition time for the alcohol was 2.5 hours and the total reflux time 6 hours.

(9) As in (8), but the total reflux time increased to 10 hours.

(10) The cyclohexanol after drying over sodium had: b.p. 161°, η_D^{25} 1.4643.

(11) The addition time for the alcohol was reduced to 1 hour and the total reflux time to 4 hours.

(C) T.2256

(i) T.2223 (35 g), in a 100 ml flask fitted with a side arm and a wide bore reflux condenser, was gently refluxed on an oil bath. The addition of ammonium fluoride (10 g = 40% excess) (dried azeotropically with carbon tetrachloride) was made in small amounts over a period of twenty minutes. Extraction of the cooled reaction mixture with ether (50 ml) followed by fractionation gave:-

(a) T.2255, b.p. 62°, η_D^{25} 1.3387. Yield 2.9 g (15%).

(b) T.2256, b.p. 127°, η_D^{25} 1.3789. Yield 12.0 g (38%). Found: C 50.8 H 10.8 F 12.0. Calc. for $C_7H_{17}OFSi$: C 51.2 H 10.4 F 11.6%.

(c) T.2257, b.p. 64°/12 mm, η_D^{25} 1.4012. Yield 8.6 g (22%).

(ii) The silane "di-di" mixture from diethyl dichloro silane (20.4 g = 0.13 moles) and T.2255 (16.0 = 0.13 moles), together with benzene (80 ml) was placed in a 200 ml flask fitted in a dropping funnel, condenser and stirrer. Isopropanol (16.2 g = 0.27 moles) was dropped into the refluxing solution over a period of one hour. After the final addition of the alcohol the system was refluxed for a further hour and then fractionated to give:-

(a) T.2256 (impure), b.p. 125° - 127°, η_D^{25} 1.3833. Yield 6.4 g (15%). Found: C 52.5 H 10.5. Calc. for $C_7H_{17}OFSi$: C 51.2 H 10.4%.

(b) T.2222, b.p. 156°, η_D^{25} 1.4116. Yield 5.0 g (21%).

(c) T.2257, b.p. 59°/10 mm, η_D^{25} 1.4014. Yield 9.4 g (36%).

(D) T.2238

This compound was obtained in 35% yield by the fluorination of T.2223 with ammonium fluoride in the same manner as used in the preparation of T.2256. The product had b.p. 141°, η_D^{25} 1.3733. Found: C 49.5 H 10.1 F 9.6. $C_8H_{19}O_2FSi$ requires: C 49.5 H 9.9 F 9.8%.
Fluorination of T.2223 with antimony trifluoride gave ethyl difluoro chloro silane, b.p. 27°. (Booth and Carnell (7)).

(E) The 2-fluoroethoxy substituted methyl and ethyl silanes were prepared by the standard method of preparation of the silane esters (see 2, A). Table VII shows the results of these experiments.

Notes

(12) 2-Fluoroethanol was dried by refluxing over calcium hydride for five hours. It had b.p. 99° - 103°, n_D^{25} 1.3664. Found: C 38.0 H 8.3. Calc. for C_2H_5OF: C 37.5 H 7.9.

(13) With the oil-bath temperature at 120° the alcohol was added over a period of three hours. The system was then refluxed for a further four hours with the bath temperature at 140°.

3. The alkyl aryloxy silanes

(A) T.2245

To a stirred and refluxed solution of dimethyl dichloro silane (55 g = 0.42 mole) in ether (150 ml), dry sodium p-nitro phenate (69 g = 0.43 mole) was added in small portions over a period of two hours. After the precipitated sodium chloride had been filtered off and the solvent removed under vacuum, a thick viscous liquid remained, that solidified after standing in a refrigerator for 48 hours. The solid was extracted with the minimum quantity of methylene chloride, cooled to 0° and the product carefully precipitated with petroleum ether (40° - 60°). The material was slowly recrystallized from a mixture of ethylene dichloride and petroleum ether (80° - 100°) (ratio 1:2). T.2245 was obtained as a light-coloured crystalline solid, m.p. 79°. Yield 30 g (42% based on the phenate). Found: C 50.3 H 4.4 Si 8.0. $C_{14}H_{14}O_6N_2Si$ requires: C 50.3 H 4.2 Si 8.4%.

(B) T.2227

The reaction between ethyl trichloro silane (30 g = 0.2 moles) and sodium p-nitro phenate (96 g = 0.6 moles) in boiling benzene (300 ml) was complete in three hours. After standing overnight some p-nitro phenol, m.p. 112° (9 g) was filtered off, and the benzene removed under vacuum. The residual viscous liquid solidified after standing in a refrigerator for 48 hours. It was recrystallized from chloroform (50 ml) to give the product, T.2227, m.p. 104°. Yield 42.5 g (45%). Found: C 50.6 H 3.7 Si 5.6. $C_{20}H_{17}O_9N_3Si$ requires: C 50.9 H 3.6 Si 5.9%.

4. Alkoxy diethylamino alkyl halo silanes

(A) Diethylamino dimethyl chloro silane

In a 1-litre flask fitted with a stirrer, dropping funnel, and reflux condenser, protected by a calcium chloride tube, was placed dimethyl dichloro silane (129 g = 1.0 mole) in petrol ether (40° - 60° - 600 ml). With the stirrer in action and with no external heating or cooling diethylamine (b.p. 54.5°,

153 g = 2.1 mole) was added during one hour. After stirring for a further four hours the diethylamine hydrochloride was filtered off and the residue fractionated. The product had b.p. 151°, η_D^{25} 1.4278. Yield 90 g (55%). Found: Cl 21.5 $C_6H_{16}ClNSi$ requires: Cl 21.4%.

The substituted silane was extremely hygroscopic and fumed copiously in moist air. Also obtained from the fractionation was T.2241, b.p. 76°/17 mm, η_D^{25} 1.4322. Yield 17.5 g (8%). Found: C 59.3 H 13.2. $C_{10}H_{26}N_2Si$ requires: C 59.3 H 13.0.

(B) T.2249

Diethylamino dimethyl chloro silane (25 g) in benzene (30 cc) was gently refluxed in an oil bath with dry zinc fluoride (30 g = 100% excess) for three hours. After filtration the benzene was recovered and the residue fractionated. The product had b.p. 111° η_D^{25} 1.3888. Yield 7.1 g (46%). Found: C 47.6 H 10.9 $C_6H_{16}FNSi$ requires: C 48.3 H 10.8%. Some unchanged starting material (8 g) was also obtained.

(C) T.2239 was obtained in good yields from isopropoxy dimethyl chloro silane (30 g) and diethylamine (30 g = 5% excess). Petrol ether (40° - 60°, 300 ml) was used as solvent, and the product had b.p. 56°/17 mm, η_D^{25} 1.4094. Yield 27.3 g (74%). Found: C 57.0 H 12.3. $C_9H_{23}ONSi$ requires: C 57.1 H 12.3%.

(D) T.2237

The preparation of this compound is carried out in a similar manner to that of T.2239, from isopropoxy ethyl dichloro silane (25 g = 0.14 mole), diethyl amine (44 g = 0.6 mole) and petrol ether (40° - 60°, 300 ml). The precipitated hydrochloride was filtered off, the residue fractionated to give T.2237, b.p. 65°/1 mm, η_D^{25} 1.4355. Yield 8.5 g (25%). Found: C 59.7 H 12.7. $C_{13}H_{32}ON_2Si$ requires: C 59.9 H 12.4%.

(E) T.2240

As was also the case with diethylamino dimethyl chloro silane, T.2240 was extremely hygroscopic and the complete exclusion of moisture during the reaction was essential. The compound was prepared from isopropoxy ethyl dichloro silane (32 g = 0.17 mole) and diethylamine (25.5 g = 0.35 mole) with petrol ether (40° - 60°, 300 ml) as the solvent. The product had b.p. 82°/17 mm, η_D^{25} 1.4255. Yield 24.8 g (65%). Found: Cl 15.9 $C_9H_{22}OClNsi$ requires: Cl 15.9%.

(F) T.2235, was obtained from the reaction of diethylamine (14.6 g = 0.2 mole) and diisopropoxy ethyl chloro silane (20.7 g = 0.1 moles) in ether (200 ml). The product had b.p. 87°/12 mm, η_D^{25} 1.4133. Yield 14.6 g (60%). Found: C 58.4 H 12.1. $C_{12}H_{29}O_2NSi$ requires: C 58.3 H 11.8.

(G) T.2252

(a) Triethoxy chloro silane was obtained in 38% yields by the method of Schumb and Stevens (21) from silicon tetrachloride and ethanol. Ether was used as the solvent and the product had b.p. 69°/32 mm, η_D^{25} 1.3878.

(b) The reaction between triethoxy chloro silane (15 g = 0.075 mole) and diethylamine (12 g = 0.16 mole), in boiling petrol ether (40° - 60°, 200 ml) was complete in 30 minutes. Fractionation of the residue obtained after filtration gave the product b.p. 87°/16 mm, η_D^{25} 1.4027. Yield 8.4 g (48%). Found C 51.0 H 10.9. $C_{10}H_{25}O_3NSi$ requires: C 51.0 H 10.7%.

5. Isopropoxy isopropylamino dimethyl silane, T.2254

The slow addition of isopropylamine (b.p. 35°, 23 g = 0.39 mole) to a stirred solution of isopropoxy dimethyl chloro silane (30 g = 0.195 mole) gave a heavy precipitate of isopropylamine hydrochloride. After refluxing for thirty minutes the reaction mixture was cooled, and the hydrochloride precipitate filtered from the solution. Fractionation of the residue gave T.2254, b.p. 51°/20 mm, η_D^{25} 1.4000. Yield 27 g (78%). Found: C 54.4 H 12.0. $C_8H_{21}ONSi$ requires: C 54.8 H 12.1%.

6. Sym. diisopropoxy tetramethyl disilazane, T.2258

Isopropoxy dimethyl chloro silane (35 g = 0.23 mole) dissolved in ether (300 ml) was placed in a 1 litre flask, fitted with a stirrer, gas inlet and reflux condenser. With the solution under reflux and the stirrer in action, ammonia (dried over caustic pellets) was bubbled through the reaction mixture for six hours. After the precipitated ammonium chloride had been removed by filtration, the residue was fractionated to yield pure T.2258, b.p. 78°/10 mm, η_D^{25} 1.4097. Yield 18.7 g (66%). Found: C 48.2 H 10.8. $C_{10}H_{27}O_2NSi_2$ requires: C 48.2 H 10.9%.

7. Isopropoxy diacetylamino dimethyl silane, T.2244

(a) Diacetimide was prepared by the method of Polya and Tardrew (32), from acetic anhydride and acetamide. After recrystallization from petrol ether (40° - 60°) it had m.p. 78°.

(b) With the temperature of the reaction mixture maintained at 110°, sodium (2.75 g = 0.12 moles) was added slowly, over a period of one hour, to a stirred solution of diacetimide (12.8 g = 0.126 moles) in toluene (110 ml). The reaction to form toluene-insoluble sodium diacetimide was complete in about an hour. The temperature of the reaction mixture was lowered to 90° and isopropoxy dimethyl chloro silane (20 g = 0.13 mole) added to the mixture. After heating had been maintained for a further hour, the precipitated sodium chloride was filtered off and the product obtained by fractionation. It had b.p. 95°/15 mm, η_D^{25} 1.4237. Yield 13.8 g (53%). Found: C 49.6 H 8.8. $C_9H_{19}O_3NSi$ requires: C 49.7 H 8.8%.

8. The alkyl alkoxy disiloxanes

(A) T.2251

To a stirred solution of isopropoxy dimethyl chloro silane (30.5 g = 0.2 mole) in pyridine (20.0 g = 0.25 mole), cooled to 0°, water (30 ml) was added dropwise over a period of thirty minutes. Ether (25 ml) was added, the upper layer separated and then washed with two 25 ml portions of 15% sodium chloride solution. After drying over calcium chloride for eighteen hours, fractionation gave the product b.p. 66°/14 mm, η_D^{25} 1.3890. Yield 20.7 g (83%). Found: C 47.7 H 10.3. $C_{10}H_{26}O_3Si_2$ requires: C 48.0 H 10.5%.

(B) T.2253

The method of preparation was similar to that of T.2251. T.2253 was obtained from diisopropoxy ethyl chloro silane (19 g = 0.09 mole), pyridine (7.9 g = 0.1 mole) and water (20 ml). It had b.p. 82°/1 mm, η_D^{25} 1.4020. Yield 9 g (55%). Found: C 51.9 H 10.4. $C_{16}H_{38}O_5Si_2$ requires: C 52.4 H 10.4%.

(C) T.2250

This compound was prepared by the method of Peppard, Brown and Johnson (24) from triethoxy chloro silane. It had b.p. 93°/2 mm (235°/750), η_D^{25} 1.3897. Yield 63%. Found: C 42.0 H 8.8. Calc. for $C_{12}H_{30}O_7Si_2$: C 42.1 H 8.8%.

APPENDIX II

Analytical Methods

1. Micro-carbon and hydrogen determinations were carried out in the normal manner. A boat of silver vanadate in the combustion tube appeared to assist the breakdown of the organo-silicon compounds during combustion.

2. Chlorine was estimated by Vohlard's method after the silicon compound had been hydrolysed with cold normal caustic soda.

3. Fluorine was estimated acidimetrically by hydrolysing the Si-F bonds with cold standard alkali for fifteen hours, and titrating the excess alkali with standard acid.

4. The wet oxidation method of Hyde and De Long (33) was used for the estimation of silicon in the solid organo-silanes.

TABLE VI

Silane	Alcohol	Solvent	Product	b.p.	n_D^{25}	Yield	Notes	Found % C	Found % H	Found % Cl	Required % C	Required % H	Required % Cl
Et_2SiCl_2 78.5 g = 0.5 mole	$(CH_3)_2CHOH$ 33 g = 0.55 mole	Benzene 50 ml	(a) $Et_2Si(OCH(CH_3)_2)Cl$ T 2222	156°	1.4121	74 g (81%)	7,8	-	-	19.4	-	-	19.6
			(b) $Et_2Si[OCH(CH_3)_2]_2$ T 2257	175° 65°/ 14 mm	1.4013	6.7 g (7%)	8	58.3	12.1	-	58.7	11.9	-
$EtSiCl_3$ 130 g = 0.8 mole	$(CH_3)_2CHOH$ 54 g = 0.9 mole	Benzene 100 ml	$Et(Cl)Si(OCH(CH_3)_2)Cl$	138°	1.4083	91 g (63%)	8	-	-	38.0	-	-	38.3
EtSiCl 96 g = 0.6 mole	$(CH_3)_2CHOH$ 75 g = 1.25 mole	Benzene 100 ml	(a) $Et(OCH(CH_3)_2)Si(Cl)OCH(CH_3)_2$ T 2223	165°	1.3982	73 g (60%)	9	-	-	17.2	-	-	16.8
			(b) $EtSi[OCH(CH_3)_2]_3$	71°/ 14 mm	1.3920	26 g (20%)	9	56.2	11.3	-	65.4	11.2	-
Et_2SiCl_2 20 g = 0.13 mole	$C_6H_{11}OH$ 13 g = 0.13 mole	Benzene 30 ml	$Et_2Si(Cl)OC_6H_{11}$ T 2225	67°/ 2 mm	1.4504	19.4 g (71%)	8,10	54.8	9.7	16.1	54.4	9.6	16.1

TABLE VI (Cont'd.)

Silane	Alcohol	Solvent	Product	b.p.	η_D^{25}	Yield	Notes	Found % C	Found % H	Found % Cl	Required % C	Required % H	Required % Cl
$EtSiCl_3$	$C_6H_{11}OH$	Benzene	Et, Cl > $Si(OC_6H_{11})_2$	106°/ 0.5 mm	1.4622	16.5 g	10,11	-	-	12.3	-	-	12.2
20 g = 0.12 mole	25 g = 0.25 mole	30 ml											

T 2224

TABLE VII

Silane	Alcohol	Solvent	Product	b.p.	η_D^{25}	Yield	Notes	Found % C	Found % H	Found % Cl	Required % C	Required % H	Required % Cl
Me_2SiCl_2	T 1904 FCH_2CH_2OH	-	(a) $Me_2Si(OCH_2CH_2F)Cl$ T 2247	126°/ 48°/ 42 mm	1.3951	45 g (29%)	12,13	31.1	6.7	22.5	30.7	6.4	22.6
129 g = 1.0 mole	64 g = 1.0 mole		(b) $Me_2Si(OCH_2CH_2F)_2$ T 2248	73°/ 23 mm	1.3867	38 g (21%)	13	38.5	7.7	-	39.1	7.7	-
Et_2SiCl_2	T 1904	Benzene	$Et_2Si(OCH_2CH_2F)Cl$ T 2229	61°/ 14 mm	1.4137	8.2 g (30%)	11	-	-	19.3	-	-	19.2
25 g = 0.16 mole	10.2 g = 0.16 mole	30 ml											
Et_2SiCl_2	T 1904	Toluene	$Et_2Si(OCH_2CH_2F)_2$ T 2236	87°/ 15 mm	1.4022	14.7 g (45%)	11	45.7	9.0	-	45.3	8.6	-
25 g = 0.16 mole	20.4 g = 0.32 mole	30 ml											
$EtSiCl_3$	T 1904	Benzene	(a) $EtSi(OCH_2CH_2F)_2Cl$ T 2228	66°/ 2 mm	1.4017	4.7 g (18%)	11	32.8	6.2	16.2	32.9	6.0	16.2
20 g = 0.12 mole	15.8 g = 0.25 mole	50 ml	(b) $EtSi(OCH_2CH_2F)_3$ T 2226	90°/ 2 mm	1.3947	8.0 g (28%)	11	38.5	7.0	-	39.0	7.0	-

BIBLIOGRAPHY

1. Kipping. Proc. Chem. Soc. 20, 15 (1904).
2. Kipping. J. Chem. Soc. 95, 302 (1909).
3. Friedel and Crafts. Ann. 136, 203 (1865).
4. Emeléus and Wilkins. J. Chem. Soc. 454 (1944).
5. Wilkins. J. Chem. Soc. 2727 (1951).
6. McCusker and Greene. J.A.C.S. 70, 2807 (1948).
7. Booth and Carnell. J.A.C.S. 68, 2650 (1946).
8. Sowa. C.A. 44, 3008 (1950). U.S.P. 2, 477, 704.
9. Marans, Sommer and Whitmore. J.A.C.S. 73, 5127 (1951).
10. Sartori. Chem. Reviews 48, 240 (1951).
11. Schrader. B.I.O.S. Final Report No. 714.
12. Perry. P.T.P. No. 166. The Chemistry of the Alkylfluorophosphonites and Related Compounds. Part XI. The Mechanism of the "Di-Di" Reaction.
13. Eaborn. J. Chem. Soc. 2846 (1952).
14. Frost. Can. J. Chem. 29, 1075 (1951).
15. Larsson and Smith. Acta. Chem. Scand. 3, 487 (1949).
16. Anderson, J.A.C.S. 74, 1421 (1952).
17. Johansson. C.A. 42, 922 (1948). U.S.P. 2, 429, 883.
18. Michaelis. Ann. 326, 129 (1903).
19. Joffe and Post. J. Org. Chem. 14, 421 (1949).
20. Rosnati. Gazz. chem. ital. 78, 516 (1948).
21. Schumb and Stevens. J.A.C.S. 69, 726 (1947).
22. Kraus and Nelson. J.A.C.S. 56, 195 (1934).
23. Sauer. J.A.C.S. 68, 241 (1946).
24. Peppard, Brown and Johnson. J.A.C.S. 68, 70 (1946).

25. Ford-Moore. P.T.P. No. 212. The Chemistry of the Alkylfluorophosphonites and Related Compounds. Part XVII. Pyrophosphonates and Mixed Anhydrides.

26. Eaborn. J. Chem. Soc. 2755 (1949).

27. Wolinski, Tieckelmann and Post. J. Org. Chem. 16, 395 (1951).

28. Speier. C.A. 46, 7582 (1952). U.S.P. 2, 582, 568.

29. Karasch, Jensen and Weinhouse. J. Org. Chem. 14, 429 (1949).

30. Gilman, Wilkinson, Fishel and Meyers. J.A.C.S. 45, 150 (1923).

31. Andrianov. J. Gen. Chem. (U.S.S.R.) 16, 487 (1946).

32. Polya and Tardrew. J. Chem. Soc. 1081, (1948).

33. Hyde and De Long. J.A.C.S. 63, 1194 (1941).

See also (a) Eaborn, J.C.S. 494 (1953).

(b) Gelman and Dunn, Chem. Reviews 52, 77 (1953).

ADDENDUM 1 TO
PORTON TECHNICAL PAPER 323

DATE 24 FEB 1953

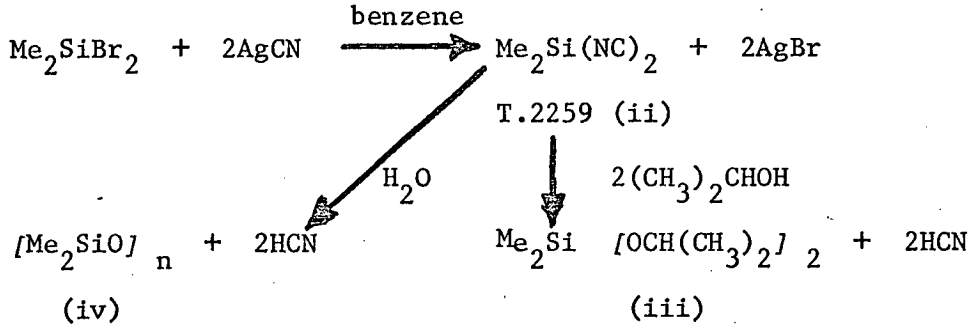
The silicon analogues of some organo-phosphorus compounds

Methyl isocyano silanes

Discussion

Although several experiments on the substitution of the chlorine group of the alkyl alkoxy chloro silanes by a cyano (or isocyano) group have been carried out (see p.4.15 section 10) no pure compounds have been isolated. However following a recent report by McBride and Beachell (1) that the methyl isocyano silanes are apparently quite toxic, dimethyl diisocyano silane has been prepared and its vapour toxicity against small animals assessed.

The alkyl chloro silanes are unreactive towards silver cyanide, but the corresponding bromo compounds react readily to form the isocyano silanes. The reasons for ascribing the isocyano structure to the new compounds in preference to the normal cyano structure have been fully reported by McBride and Beachell (1). Bromination of the methyl phenyl silanes (prepared by a Grignard reaction with phenyl magnesium bromide on the methyl chloro silanes) with liquid bromine gives the corresponding alkyl bromo silanes.



Dimethyl diisocyano silane, T.2259 (ii) formed by the above reaction is a reactive white crystalline solid. It hydrolyses rapidly and liberates HCN. Similarly when dropped into water it reacts immediately on contact, liberating HCN and forming methyl cyclo-polysiloxane (iv). If the water is made acid or alkaline the reaction is even more vigorous. Isopropanol reacts with T.2259 without difficulty forming dimethyl diisopropoxy silane (iii), and liberating HCN in almost quantitative yields. The infrared absorption spectrum of T.2259 agrees, in general, with that described by McBride and Beachell (1).

Toxicological Results

The sensitivity of T.2259 towards hydrolysis and its reactivity towards organic hydroxyl groups, precludes any attempt to assess its toxicity by injection via the subcutaneous or intravenous routes into test animals. However, since T.2259 is thermally quite stable and can be assessed and compared with normal pressure, its vapour toxicity can be assessed and compared with that of hydrogen cyanide under the same experimental conditions. The results of the chamber trials of T.2259 and HCN are given in Table 1.

TABLE 1

Compound	Weight of sample dispersed into chamber (g)	Average concentration of HCN (mg/m^3)	% Recovery	Death Rate (Rats) (Exposure time = 30 min)
T 2259	7.7	225	65%	8/10
HCN	3.5	211	66%	7/10

From these results it appears that the toxicity of T.2259 is due mainly to the contained hydrogen cyanide, the latter being no doubt liberated by the moisture in the atmosphere of the chamber. This result is not unexpected and it confirms the results obtained with the 2-fluoro ethyl and p-nitrophenyl esters of the alkyl halo silanes as described in P.T.P. 323. From the point of view of a potential chemical warfare agent, the methyl isocyano silanes appear to be most unsuitable since they are so readily decomposed by atmospheric moisture.

Acknowledgements

The assistance of J.W. Blackburn during the toxicological assessments and B.J. Purser for carrying out the sampling and estimations required during the chamber trials is gratefully acknowledged.

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EXPERIMENTAL RESULTS

A. Preparation and Reactions of T.2259

(i) The experimental procedure in general, followed that described by McBride and Beachell (1), although in some cases modification of the methods reported gave an increased yield of products.

(ii) Dimethyl diphenyl silane

This material was prepared from dimethyl, dichloro silane and phenyl magnesium bromide, using dry ether as the solvent. The yield of product, b.p. 138°-140°/14 mm, n_D^{25} 1.5580, was 65%.

(iii) Dimethyl dibromo silane

Dimethyl diphenyl silane (139 g = 0.65 mole), placed in a three-necked, 1-litre flask, fitted with a stirrer, dropping funnel and reflux condenser, was cooled to 0° and treated with liquid bromine (208 g = 1.3 mole) over a period of two hours. After the addition of the bromine, the mixture was kept at 60°-70° for 24 hours, and then styrene added dropwise until the bromine colour had just disappeared (12.1 ml). Fractionation gave dimethyl dibromo silane, b.p. 111°, n_D^{25} 1.4716. Yield 87 g (61%). Bromobenzene, b.p. 156°, was recovered in a yield of 64%.

(iv) T.2259

Dimethyl dibromo silane (85 g = 0.39 mole) in dry benzene (350 ml), was placed in a 1-litre flask fitted with a side arm and a reflux condenser. After the slow addition of dry silver cyanide (115 g = 0.85 mole) over a period of one hour, the mixture was refluxed for a further six hours. The yellow silver salts were filtered from the reaction mixture, washed several times with hot benzene, and the combined filtrates fractionated to give dimethyl diisocyano silane, T.2259, b.p. 110°/100 mm (169°/760 mm). Yield 28 g (65%). After recrystallization from dry ether the product had m.p. 83°-84°. Found: CN (by a Liebig titration) 46.9, 47.0. Calc. for $C_4H_6SiN_2$: CN, 47.2%.

(v) Reaction of T.2259 with isopropanol

In a 250 ml flask, fitted with a dropping funnel and reflux condenser, was placed T.2259 (5.5 g = 0.05 mole) in dry ether (150 ml). The condenser was connected to a gas absorption apparatus containing normal sodium hydroxide (50 ml). After dry isopropanol (6 g = 0.1 mole), in ether (20 ml), had been added dropwise over a period of twenty minutes, the mixture was gently refluxed for one hour, cooled, and shaken with the sodium hydroxide from

the absorption apparatus, in order to remove the dissolved HCN. This procedure was repeated with three further portions of alkali and finally with distilled water. The combined washings were made up to 250 ml, and assayed for HCN to give a recovery of 2.45 g (91%). After drying over calcium chloride the ether solution was fractionated to give dimethyl diisopropoxy silane, b.p. 131°-132°, n_D^{25} = 1.3847. Yield 6.55 g (86%).

B. Assessment of vapour toxicity of T.2259

The assessment of the vapour toxicity of T.2259 and HCN was carried out in an 11 m^3 chamber in the Physiology Section. T.2259 was dispersed into the chamber by vapourizing it from a hot plate into a hot air stream, and the HCN cloud was established by means of a Neale disperser. Estimation of the vapour concentration in the chamber was carried out by sampling through "dimple" type bubblers (containing normal sodium hydroxide), at 10 l/min, and assaying the cyanide present by means of a Liebig titration. As the test animals (white, 200 g male rats) were exposed for a period of 30 minutes, three successive, ten minute samples of the cloud concentration were taken, and the dose of toxic agent received by the animals calculated as the average of these three assays.

REFERENCES

1. McBride and Beachell. J.A.C.S. 74, 5247 (1952).

APPENDIX 5 ORGANOTITANIUM COMPOUNDS

5a The Preparation and Polymerization of Mixed Tetra-orthoesters of Titanium.
P. DUNN. *Aust. J. Appl. Sci.*,
13, No. 4, 458-463 (1959). 5.2 - 5.8

5b Addition Compounds of Titanium.
P. DUNN. *Aust. J. Chem.*,
13, No. 2, 225-229 (1960). 5.9 - 5.14

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THE PREPARATION AND POLYMERIZATION OF MIXED TETRAORTHO-ESTERS OF TITANIUM

By P. DUNN

Appendix 5a

5.2 - 5.8

THE PREPARATION AND POLYMERIZATION OF MIXED TETRAORTHOESTERS OF TITANIUM

By P. DUNN*

[*Manuscript received July* 16, 1959]

Summary

A method based on the stepwise reaction of different alcohols with titanium tetrachloride, and the use of ammonia to remove the liberated hydrogen chloride, has been developed for the synthesis of mixed methyl butyl esters of titanium.

Polymeric mixed esters of titanium have been prepared by the partial hydrolysis of monomeric mixed methyl butyl esters, using varying amounts of water dissolved in butanol.

I. INTRODUCTION

(*a*) *Preparation*

Ammonia has been used in the pilot-plant preparation of titanium tetra-*n*-butoxide (Kraitzer, McTaggart, and Winter 1948) and the laboratory-scale preparation of several titanium tetra-alkoxides (Cullinane and Chard 1949) from titanium tetrachloride.

In these reactions the formation of the tetraorthoesters proceeds stepwise and when dichlorotitanium di-*n*-butoxide or chlorotitanium tri-*n*-butoxide is treated with butanol and ammonia, the tetra-*n*-butoxide is obtained.

The present paper describes a modification of this method, that gives mixed tetraorthoesters in good yields.

By controlled reaction of *n*-butanol with titanium tetrachloride in the presence of ammonia, solid ammonia addition compounds of the various chlorotitanium-*n*-butoxides have been obtained. These compounds on treatment with the appropriate alcohol give the mixed tetraorthoester.

Titanium monomethoxide tri-*n*-butoxide, titanium dimethoxide di-*n*-butoxide, and titanium trimethoxide mono-*n*-butoxide have been prepared by this method, and purified by fractionation. Mixed tetraorthoesters are also obtained when the alcohols are mixed initially and then reacted with titanium tetrachloride and ammonia.

Titanium monomethoxide tri-*n*-butoxide has also been prepared by the trans-esterification reaction of titanium tetra-*n*-butoxide and methanol. However the introduction of a second methoxy group to form titanium dimethoxide di-*n*-butoxide by this method does not readily occur. The trans-esterification reaction is reversible since titanium tetramethoxide and excess *n*-butanol react to form titanium tetra-*n*-butoxide.

Bradley, Hancock, and Wardlaw (1952) have shown that a radical interchange reaction occurs when an excess of titanium tetrachloride is heated with titanium

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tetra-alkoxide. Similarly it has now been found that equimolar quantities of titanium tetramethoxide and titanium tetra-*n*-butoxide undergo an interchange reaction when heated under reduced pressure to give titanium dimethoxide di-*n*-butoxide.

Teichner (1953) has described a method for the preparation of titanium tetramethoxide from titanium tetrachloride, methanol, and ammonia, and this method has now been modified to give good yields of the tetraorthoester.

(*b*) *Polymerization*

The polymerization of titanium esters may be carried out either by thermal or by chemical means such as acetic acid or other organic acids. The use of water as a hydrolysing agent has been investigated by Boyd (1951) and Winter (1953), who postulate that water reacts with the titanium esters to form, in the first instance, hydroxy compounds which condense with the liberation of part of the water. This is then available for further reaction.

In general terms the reaction may be written as:

$$\mathrm{Ti(OR)_4} + n\ \mathrm{H_2O} \longrightarrow \mathrm{TiO_n(OR)_{4-2n}} + 2n\ \mathrm{ROH}.$$

However with reactions involving more than 0·5 mole-equiv of water the polymerization does not go to completion, and in some cases unreacted water can be recovered from the system.

The reaction of 0·5 mole-equiv of water with titanium trimethoxide mono-*n*-butoxide produces the symmetrical ester of polyorthotitanic acid, namely *sym.*-tetramethoxy di-*n*-butoxy dititanoxane. Both Boyd (1951) and Winter (1953) have shown that the reaction product from titanium tetra-*n*-butoxide and 0·5 mole-equiv of water is hexa-*n*-butoxy dititanoxane. Since the reactivity of the higher alkyl titanates with water is less than the lower homologues, it might be expected that during the polymerization the methoxy groups of the ester should be eliminated preferentially to the butoxy groups. Thus the 1·0 mole polymer from titanium trimethoxide mono-*n*-butoxide should be the long straight-chain polymer methoxy butoxy polytitanoxane with a molar ratio CH_3O:TiO_2 value 1·0. During the polymerization however butoxy groups as well as methoxy groups are eliminated and the molar ratio CH_3O : TiO_2 is 1·24. After hydrolysis with 6·0 mole-equiv of water, some methoxy groups are still present in the polymer.

Analytical data on organotitanium polymers formed by polymerizing different monomers with varying amounts of water in butanol are given in Table 1.

Polymers formed by the hydrolysis of titanium dimethoxide di-*n*-butoxide and titanium methoxide tri-*n*-butoxide also confirm the observation that methoxy groups are not removed preferentially to butoxy. As the degree of polymerization increases, the molar ratio CH_3O : TiO_2 decreases towards zero, and the titanium dioxide content approaches that found for the polymers obtained from titanium tetra-*n*-butoxide.

Boyd (1951) observed that gels could be formed by allowing solutions of titanium alkoxides to stand exposed to the atmosphere but he could not produce them under experimental conditions. Under carefully controlled conditions polymeric

TABLE 1

ANALYTICAL DATA ON ORGANOTITANIUM POLYMERS

Monomer		$(CH_3O)_3Ti(OC_4H_9)$		$(CH_3O)_2Ti(OC_4H_9)_2$		$(CH_3O)Ti(OC_4H_9)_3$		$(C_4H_9O)_4Ti$
Mole Polymer	Drying Temperature (°C)	TiO_2 Found (%)	Mole Ratio CH_3O/TiO_2	TiO_2 Found (%)	Mole Ratio CH_3O/TiO_2	TiO_2 Found (%)	Mole Ratio CH_3O/TiO_2	TiO_2 Found (%)
0	—	37·2	3·00	31·2	2·00	26·7	1·00	23·5
0·5	40	41·8	1·97	34·0	1·14	30·4	0·66	29·5
1·0	45	47·0	1·25	42·0	0·65	39·1	0·38	37·8
1·5	45	51·9	0·76	51·0	0·38	50·1	0·23	49·0
2·0	45	55·8	0·49	55·9	0·25	54·6	0·16	55·0
2·5	50	57·6	0·31	57·7	0·17	57·6	0·11	57·7
3·0	50	59·5	0·23	59·9	0·12	59·3	0·09	59·6
4·0	50	60·4	0·12	60·8	0·08	60·3	0·06	61·7
6·0	50	62·2	0·08	62·9	0·05	61·9	0·04	62·9

mixed esters of titanium will gel hydrocarbon solvents. The degree of polymerization and the molar ratio CH_3O : TiO_2 for various polymers formed at the instant of gelation of the hydrocarbon are given in Table 2. To attain gelation of hexane there is a minimum amount of water required for the polymerization reaction. The polymers that are most suitable for the gelling reaction are those with the highest methoxy content. This is consistent with the observation that an increase in the methoxy content of a polymer results in a decrease in the general solubility of the material.

TABLE 2

GELATION OF HYDROCARBONS BY ORGANOTITANIUM POLYMERS

Monomer	Concentration of Monomer in Hexane (5°C; w/w %)	Mole Polymer at Point of Gelation	Molar Ratio CH_3O/TiO_2 of Polymer
$(C_4H_9O)_4Ti$	23·4	3·20	0
$(C_4H_9O)_3Ti(OCH_3)$	25·5	1·55	0·22
$(C_4H_9O)_2Ti(OCH_3)_2$	25·0	1·32	0·48
$(C_4H_9O)Ti(OCH_3)_3$	26·0	1·08	1·20
$Ti(OCH_3)_4$	Insoluble	—	—

II. EXPERIMENTAL

(*a*) *Analytical Methods*

Titanium dioxide was determined by hydrolysing samples with aqueous ammonia. In the case of polymeric titanium compounds, a further reaction with concentrated nitric acid was necessary before the residue was ignited to titanium dioxide. Samples were dissolved in dilute nitric acid and volumetric methods used for determining chloride. Methoxyl was determined spectrophotometrically using a modification of the method described by Mathers and Pro (1955).

(*b*) *Tetraorthoesters*

(i) *Titanium Monomethoxide Tri-*n*-butoxide.*—Anhydrous *n*-butanol (222·3 g; 3·0 moles) was added dropwise to a solution of titanium tetrachloride (189·7 g; 1·0 mole) in dry hexane (400 ml) with water cooling. After the addition, hexane (500 ml) was added and the solution heated at 60°C for 8 hr. Dry ammonia was blown through the cooled and vigorously stirred solution for 4 hr (that is, until the solution was saturated) and anhydrous methanol (32 g; 1·0 mole) then added. After refluxing for 4 hr, the flask was cooled and the precipitated ammonium chloride removed by filtration. The solvent was removed under vacuum and the product fractionated, b.p. 153–154°C/0·4 mm. The yield based on the tetrachloride was 70 per cent. and $n_D^{20} = 1·5068$ (Found: TiO_2 equiv, 26·9; CH_3O, 10·3%. Calc. for $C_{13}H_{30}O_4Ti$: TiO_2 equiv, 26·9; CH_3O, 10·4%).

The clear viscous liquid solidified on standing for 24 hr and was then recrystallized from anhydrous butane (at −20°C) to give fine white needle-like crystals, m.p. 39·5–40·5°C.

To titanium tetra-*n*-butoxide (1·0 mole) (b.p. 143°C/0·3 mm, $n_D^{20} = 1·4938$) in hexane (400 ml) anhydrous methanol (1·1 moles) was added and the solution refluxed for 2 hr. Removal of the solvent under vacuum followed by fractionation gave the product, titanium monomethoxide tri-*n*-butoxide, $n_D^{20} = 1·5070$ in a yield of 81% (Found: TiO_2 equiv, 26·7; CH_3O, 10·1%).

(ii) *Titanium Dimethoxide Di-*n*-butoxide.*—Titanium tetrachloride (663 g; 3·5 moles) in dry hexane (2000 ml) was treated dropwise with *n*-butanol (518 g; 7·0 moles) over a period of 3 hr, the temperature of the solution being kept below 25°C. The solution was heated to 55°C for 2 hr while a rapid stream of dry nitrogen was passed through the liquid. Hexane (1200 ml) was added, the temperature maintained at 40°C, and dry ammonia bubbled into the solution. When saturated, methanol (224 g; 7·0 moles) in hexane (500 ml) was added, and the solution stirred at 40°C for a further 2 hr, the precipitated ammonium chloride was removed by filtration and washed with hexane. The combined filtrates and washings were stripped down under vacuum, and the product fractionated at 157°C/0·3 mm. The pale yellow viscous liquid (572 g, yield 68%) had $n_D^{20} = 1·5184$ (Found: TiO_2 equiv, 31·3; CH_3O, 24·4%. Calc. for $C_{10}H_{24}O_4Ti$: TiO_2 equiv, 31·2; CH_3O, 24·2%).

Titanium tetra-*n*-butoxide (68·0 g; 0·2 mole) and titanium tetramethoxide (34·4 g; 0·2 mole) were refluxed under vacuum for 2 hr and then fractionated. The product titanium dimethoxide di-*n*-butoxide had b.p. 156°C/0·2 mm, $n_D^{20} = 1·5178$ (yield 81%) (Found: TiO_2 equiv, 31·0%).

(iii) *Titanium Trimethoxide Mono-*n*-butoxide.*—To a cooled solution of titanium tetrachloride (136 g; 0·7 mole) in dry hexane (600 ml), *n*-butanol (51·8 g; 0·7 mole) was added, and the solution heated at 40°C for 2 hr. After cooling to 15°C, hexane (600 ml) was added and the solution saturated with ammonia. The yellow ammonia addition product was heated to 40°C and treated with methanol (67·2 g; 2·1 moles). The product was recovered by filtration and fractionation at 165–166°C/0·6 mm. The yield of colourless viscous oil was 61% and $n_D^{20} = 1·5362$. On long standing, the liquid solidified to a white wax-like product of indefinite melting point (Found: TiO_2 equiv, 37·2; CH_3O, 43·4%. Calc. for $C_7H_{18}O_4Ti$: TiO_2 equiv, 38·3; CH_3O, 43·5%).

(iv) *Titanium Tetramethoxide.*—To a cooled and stirred solution of titanium tetrachloride (379 g; 2·0 moles) in dry redistilled toluene (2000 ml), methanol (320 g; 10·0 moles) was added. The solution was heated at 90°C for 4 hr, toluene (500 ml) added, and the hot solution saturated with dry ammonia. Surplus methanol was removed by distillation, and the solution then refluxed for 1 hr. After removal of the ammonium chloride by filtration of the hot solution, the filtrate was cooled to 0°C for 24 hr. The pale yellow crystalline tetramethoxide was recovered by filtration and recrystallized from toluene. The product had m.p. 216–217°C, and was obtained in a yield of 64% (Found: TiO_2 equiv, 46·4; CH_3O, 71·3%. Calc. for $C_4H_{12}O_4Ti$: TiO_2 equiv, 46·5; CH_3O, 72·1%).

(c) *Polymerization of Titanium Tetraorthoesters*

The polymerization of the individual monomers was carried out under standardized conditions; the only variation between experiments being the final drying temperature. The following preparation of the 0·5 mole polymer from titanium trimethoxide mono-*n*-butoxide is an example of the general procedure.

Titanium trimethoxide mono-*n*-butoxide (21·4 g; 0·1 mole) in dry hexane (100 ml) was cooled to 5°C and treated dropwise with a 10% solution of water (0·9 g; 0·05 mole) in butanol. After the addition, the stirred solution was heated on a water-bath at 40°C for 3 hr. The solvent was removed under a water vacuum, and the polymer dried (at 5 mm pressure) for 8 hr at a temperature of 40°C. The product, a pale viscous liquid, was obtained in a yield of 97% (Found: TiO_2 equiv, 41·8; CH_3O, 31·9%. Calc. for $C_{12}H_{30}O_7Ti_2$: TiO_2 equiv, 41·7; CH_3O, 32·5%). The product corresponds to the true half mole polymer from titanium trimethoxide mono-*n*-butoxide, namely, sym.-*tetramethoxy di-*n*-butoxy dititanoxane.*

In reactions where polymerization causes gelation of the hydrocarbon solvent, no change in procedure was adopted. In the preparation of polymers using greater than 1·5 mole-equiv of water, some unreacted water was obtained. This was removed from the polymer during the final vacuum drying stage.

III. Acknowledgment

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IV. References

Boyd, T. (1951).—*J. Polym. Sci.* **7**: 591.
Bradley, D. C., Hancock, D. C., and Wardlaw, W. (1952).—*J. Chem. Soc.* **1952**: 2773.
Cullinane, N. M., and Chard, S. J. (1949).—*Nature* **164**: 710.
Kraitzer, I. C., McTaggart, F. K., and Winter, G. (1948).—*J. Coun. Sci. Industr. Res. Aust.* **21**(4): 328–46.
Mathers, A. P., and Pro, M. J. (1955).—*Analyt. Chem.* **27**: 1662.
Teichner, S. (1953).—*C.R. Acad. Sci. Paris* **237**: 900.
Winter, G. (1953).—*J. Oil Col. Chem. Ass.* **36**: 689.

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ADDITION COMPOUNDS OF TITANIUM

By P. Dunn

Appendix 5b

5.9 - 5.14

ADDITION COMPOUNDS OF TITANIUM

By P. DUNN*

[*Manuscript received August* 19, 1959]

Summary

The reaction of titanium tetrachloride, chlorotitanium alkoxides, and titanium tetra-alkoxides with ammonia and pyridine has been investigated. Solid, stable, addition complexes are formed; these react further with alcohols to give the fully substituted ester. In some of the ammonia complexes, titanium exhibits covalencies five and six.

I. INTRODUCTION

The reaction between titanium tetrachloride and ammonia has been investigated tensimetrically at low temperatures (Fowles and Pollard 1953). Their observation that titanium tetrachloride octa-ammoniate can be formed only at low temperatures has been confirmed in the present work. It has now been found that the hexa-ammoniate which forms at room temperature (Rosenheim and Schutte 1901) loses ammonia on heating in a vacuum at 120 °C and forms titanium tetrachloride tetra-ammoniate. This compound can be reconverted to the hexa-ammoniate by treatment with dry ammonia gas. Reaction of titanium tetrachloride hexa-ammoniate or tetra-ammoniate with *n*-butanol gives good yields of titanium tetra-*n*-butoxide, while treatment with water liberates all the ammonia as ammonium chloride. Andrew and Nikolskii (1953) have reported a similar reaction between ethanol and titanium tetrachloride octa-ammoniate.

Further, trichlorotitanium mono-*n*-butoxide in hexane solution reacts with gaseous ammonia at room temperature to form trichlorotitanium mono-*n*-butoxide penta-ammoniate. This compound may be converted to trichlorotitanium mono-*n*-butoxide triammoniate either by heating under vacuum or by exposure over phosphorus pentoxide. Both the penta-ammoniate and the triammoniate are insoluble in common organic solvents and react with *n*-butanol to form the tetraorthoester. With methanol the penta-ammoniate forms titanium trimethoxide mono-*n*-butoxide and this reaction has been extended to the preparation of the mixed tetraorthoesters in a one-step process from titanium tetrachloride (Dunn 1959). Water hydrolyses the ammoniates rapidly with the formation of ammonium chloride and butanol.

Similar reactions occur with monochlorotitanium tri-*n*-butoxide, which in hexane solution at 15 °C absorbs 1 mole of ammonia, and on cooling to −5 °C

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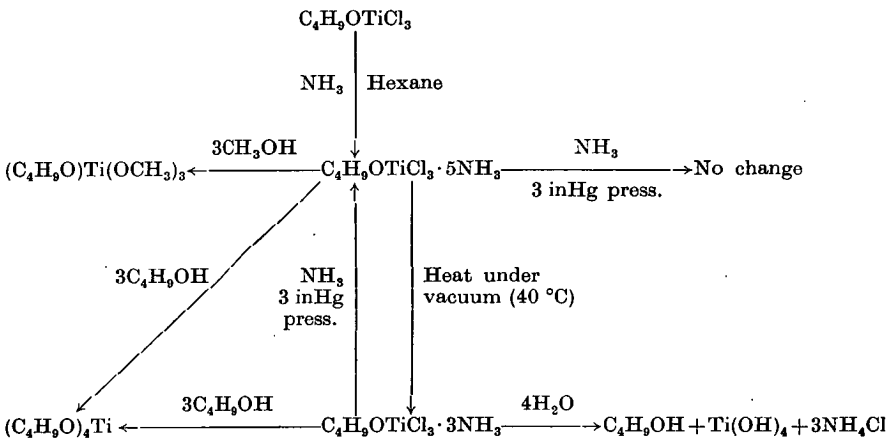
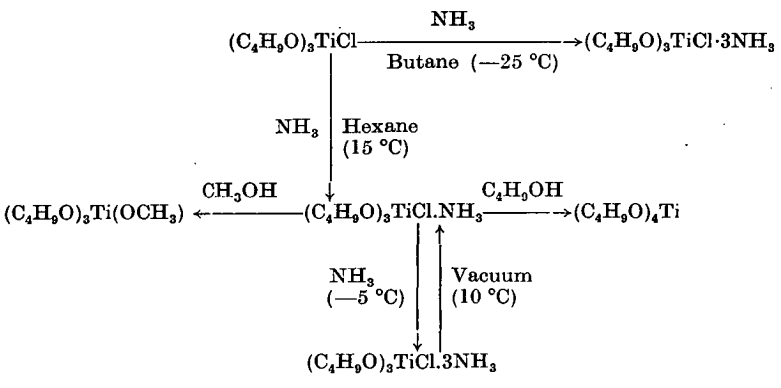
absorbs a further 2 moles. The triammoniate compound may be readily converted to monochlorotitanium tri-*n*-butoxide monoammoniate by evacuation at 10 °C. The monoammoniate is soluble in hexane.

Since dichlorotitanium di-*n*-butoxide disproportionates readily on fractionation no attempt was made to prepare the ammonia addition compounds of this material.



(I)

In boiling hexane, trichlorotitanium mono-*n*-butoxide forms an addition compound with 3 moles of pyridine. Trichlorotitanium mono-*n*-butoxide tripyridinate is soluble in hydrocarbon and chlorinated hydrocarbon solvents and does not react further with pyridine. Reaction with *n*-butanol gives titanium tetra-*n*-butoxide.



(II)

Similarly monochlorotitanium tri-*n*-butoxide reacts with 1 mole of pyridine to form the monopyridinate. This compound can be crystallized from aliphatic hydrocarbons and does not react further with pyridine. Even at reduced temperatures, no reaction was observed between pyridine and titanium tetra-*n*-butoxide.

II. Discussion

From the series of compounds prepared it can be concluded that 1 mole of ammonia is added for each mole of chlorine in the compound. Either 1, or more often, 2 moles of ammonia may also be added per mole of titanium. These are no doubt held by coordination valencies to the titanium atom. The thermal stability of the bond increases as replacement of alkoxy groups by chlorine increases.

Fowles and Pollard (1953) have examined the reaction between titanium tetrachloride and liquid ammonia at low temperatures. They concluded that an amido chloride, $Ti(NH_2)_3Cl$, and ammonium chloride are formed. In the present series of reactions of titanium tetrachloride, chlorotitanium alkoxides, and titanium tetra-alkoxides with gaseous ammonia, no ammonium chloride could be detected. The monoammoniate compound formed from monochlorotitanium tri-*n*-butoxide and gaseous ammonia is soluble in hydrocarbon solvents. The greater stability of the bond linking the ammonia and the chlorine, in contrast to the coordination bond linking the ammonia and the titanium, is evidenced by the loss of the ammonia attached to the titanium on heating.

While silicon tetrachloride can form a tetrapyridinate (Trost 1951) and titanium tetrachloride can form a dipyridinate (Piper and Rochow 1954), no evidence of tetrapyridinate formation with titanium tetrachloride was found.

Ammonia will displace pyridine from the pyridinates of titanium tetrachloride and chlorotitanium alkoxides to form the corresponding ammoniates. Thus trichlorotitanium mono-*n*-butoxide tripyridinate can be readily converted to trichlorotitanium mono-*n*-butoxide penta-ammoniate by treatment with gaseous ammonia. With trichlorotitanium mono-*n*-butoxide triammoniate and with titanium tetrachloride tetra-ammoniate it was not possible to displace the ammonia with pyridine.

III. Experimental

Chlorine was determined volumetrically after samples were hydrolysed with methanolic potash. Hydrolysis of samples with concentrated ammonia, followed by ashing, gave the titanium dioxide content. Ammonia was distilled from a sample into saturated boric acid (from a Kjeldahl apparatus) and determined volumetrically. Reactions were carried out with the careful exclusion of moisture.

(*a*) *Ammonia Addition Compounds.*

(i) *Titanium Tetrachloride Hexa-ammoniate and Titanium Tetrachloride Tetra-ammoniate.*—These compounds were prepared by Rosenheim and Schutte's (1901) method from titanium tetrachloride and dry gaseous ammonia.

Finely powdered titanium tetrachloride tetra-ammoniate was treated with dry gaseous ammonia at a pressure of 3 inHg above atmospheric for 4 hr at room temperature, the vessel being shaken continuously. Free ammonia was then removed under reduced pressure to give titanium tetrachloride hexa-ammoniate (Found: Cl, 48·5; TiO_2, 27·2; NH_3, 34·3%; mol. ratio $Cl : TiO_2$, 4·02; mol. ratio $NH_3 : Cl$, 1·48. Calc. for $C_{18}Cl_4N_6Ti$: Cl, 48·5; TiO_2, 27·3; NH_3, 35·0%).

(ii) *Trichlorotitanium Mono-*n*-butoxide Penta-ammoniate.*—Anhydrous ammonia gas was bubbled through a hexane solution of trichlorotitanium mono-*n*-butoxide, m.p. 70–72 °C, b.p. 93 °C/3 mm, at 15 °C for 3 hr. After removal of the solvent by vacuum evaporation, the produc t

was obtained in a yield of 95% (Found : Cl, 33·9 ; TiO_2, 25·6 ; NH_3, 26·4% ; mol. ratio Cl : TiO_2 3·0 ; mol. ratio NH_3 : Cl, 1·62. Calc. for $C_4H_{24}Cl_3ON_5Ti$: Cl, 34·0 ; TiO_2, 25·6 ; NH_3, 27·2%)

The triammoniate of trichlorotitanium mono-*n*-butoxide was treated with ammonia gas for 4 hr at a pressure of 3 inHg above atmospheric, the reaction vessel being shaken continuously Free ammonia was then removed under reduced pressure (Found : Cl, 33·6 ; TiO_2, 25·2 ; NH_3 27·0% ; mol. ratio Cl : TiO_2, 3·01 ; mol. ratio NH_3 : Cl, 1·66).

(iii) *Trichlorotitanium Mono-*n*-butoxide Triammoniate.*—The penta-ammoniate was heated at 40 °C for 12 hr under vacuum (1–5 mmHg press.) (Found : Cl, 37·8 ; TiO_2, 28·2 ; NH_3 18·8% ; mol. ratio Cl : TiO_2, 3·01 ; mol. ratio NH_3 : Cl, 1·04. Calc. for $C_4H_{18}Cl_3ON_3Ti$ Cl, 38·2 ; TiO_2, 28·7 ; NH_3, 18·4%).

The triammoniate was also formed by exposure of trichlorotitanium mono-*n*-butoxide penta ammoniate over phosphorus pentoxide in a vacuum desiccator for 2 days (Found : Cl, 38·2 TiO_2, 28·1 ; NH_3, 17·8% ; mol. ratio Cl : TiO_2, 3·06 ; mol. ratio NH_3 : Cl, 0·97).

(iv) *Monochlorotitanium Tri-*n*-butoxide Triammoniate.*—Monochlorotitanium tri-*n*-butoxide b.p. 164 °C/1·0 mm (Cullinane *et al.* 1952) was dissolved in dry butane at —25 °C and treated with anhydrous ammonia gas for 3 hr. The solvent was decanted and the crystalline precipitate dried by vacuum evaporation at —30 °C (Found : Cl, 9·8 ; TiO_2, 22·6 ; NH_3, 14·2% ; mol. ratio Cl : TiO_2, 0·98 ; mol. ratio NH_3 : Cl, 3·00. Calc. for $C_{12}H_{36}ClO_3N_3Ti$: Cl, 10·0 ; TiO_2, 22·6 NH_3, 14·4%).

The triammoniate was also formed by treating monochlorotitanium tri-*n*-butoxide mono-ammoniate with dry ammonia gas under a pressure of 3 inHg above atmospheric for 48 hr at a temperature of —5 °C (Found : Cl, 9·9 ; TiO_2, 22·1 ; NH_3, 13·8% ; mol. ratio Cl : TiO_2 1·01 ; mol. ratio NH_3 : Cl, 2·91).

(v) *Monochlorotitanium Tri-*n*-butoxide Monoammoniate.*—Through a solution of mono-chlorotitanium tri-*n*-butoxide in hexane, at 15 °C, dry ammonia was bubbled until the solution was saturated. The solvent and free ammonia were removed under vacuum over a period of 8 hr to give a 96% yield of product. This product was dissolved in dry hexane to give a 10% solution, and insoluble matter removed by centrifuging. After removal of the hexane under reduced pressure and at a temperature not exceeding 20 °C, the product was dissolved in dry butane and crystallized at —70 °C (Found : Cl, 10·9 ; TiO_2, 24·8 ; NH_3, 5·0% ; mol. ratio Cl : TiO_2, 0·99 ; mol. ratio NH_3 : Cl, 0·96. Calc. for $C_{12}H_{30}ClO_3NTi$: Cl, 11·1 ; TiO_2, 25·0 ; NH_3, 5·3%).

Evacuation of monochlorotitanium tri-*n*-butoxide triammoniate for 4 hr at 10 °C also gave the monoammoniate (Found : Cl, 11·0 ; TiO_2, 25·0 ; NH_3, 5·4% ; mol. ratio Cl : TiO_2, 0·99 ; mol. ratio NH_3 : Cl, 1·02).

(vi) *Titanium Tetra-*n*-butoxide Monoammoniate.*—Ammonia gas was bubbled for 3 hr through a solution of titanium tetra-*n*-butoxide in a light petroleum-ether fraction (b.p. 30–34 °C) cooled to —25 °C. The solution was then cooled to —50 °C when a white solid precipitated. Excess solvent was decanted, and the product obtained in an 82% yield by vacuum evaporation at —50 °C. Recrystallization from anhydrous butane at —70 °C gave the monoammoniate as fine white needle-like crystals (Found : TiO_2, 21·6 ; NH_3, 4·7% ; mol. ratio NH_3 : TiO_2, 1·02. Calc. for $C_{16}H_{39}O_4NTi$: TiO_2, 22·4 ; NH_3, 4·9%).

Reaction of liquid ammonia with titanium tetra-*n*-butoxide in butane at —70 °C, also gave titanium tetra-*n*-butoxide monoammoniate.

(vii) *Reaction of Ammonia Addition Compounds with Butanol.*—To a stirred suspension of titanium tetrachloride hexa-ammoniate (146 g ; 0·5 mole) in dry hexane (800 ml), at 15 °C, dry butanol (163 g ; 2·2 moles) was added over a period of 1 hr. The white hexane-insoluble ammonium chloride was filtered off and the combined filtrates and washings stripped down under vacuum and distilled. Titanium tetra-*n*-butoxide, b.p. 174 °C/3 mm, n_D^{20}=1·4933 was obtained in a yield of 70% (Found : TiO_2, 23·5%. Calc. for $C_{16}H_{36}O_4Ti$: TiO_2 23·5%).

The ammonia addition compounds of monochlorotitanium tri-*n*-butoxide and of trichloro-titanium mono-*n*-butoxide as well as titanium tetrachloride tetra-ammoniate also react with butanol in the manner described above to give titanium tetra-*n*-butoxide.

(b) Pyridine Addition Compounds

(i) *Titanium Tetrachloride Dipyridinate.*—This compound was prepared by Piper and Rochow's (1954) method from titanium tetrachloride and pyridine.

(ii) *Trichlorotitanium Mono-n-butoxide Tripyridinate.*—Five M-equiv. of pyridine was added slowly to a hexane solution of trichlorotitanium mono-*n*-butoxide at 30 °C. The product separated as a viscous liquid which solidified on cooling. After washing with hexane, and drying under reduced pressure, the light coloured free-flowing powder was obtained in a yield of 97% (Found : TiO_2, 17·8 ; Cl, 23·3% ; mol. ratio Cl : TiO_2, 2·96. Calc. for $C_{19}H_{24}Cl_3N_3OTi$: TiO_2, 17·2 ; Cl, 22·9%). The tripyridinate was also obtained when 3 instead of 5 moles of pyridine per mole of titanium tetrachloride were used.

(iii) *Monochlorotitanium Tri-n-butoxide Monopyridinate.*—Monochlorotitanium tri-*n*-butoxide was mixed with 1 M-equiv. of pyridine and the solution then cooled to —25 °C. Butane was added, until the white precipitate just dissolved, and the solution was stored for 2 days at —18 °C. The crystals of monochlorotitanium tri-*n*-butoxide monopyridinate formed after this time were separated, washed with butane, and dried. On warming to approx. 20 °C the crystals melted to a clear liquid (Found : TiO_2, 20·6 ; Cl, 9·5% ; mol. ratio Cl : TiO_2, 1·04. Calc. for $C_{17}H_{32}ClO_3NTi$: TiO_2, 20·9 ; Cl, 9·3%).

(iv) *Reaction of Pyridine Addition Compounds with Butanol.*—Titanium tetrachloride dipyridinate (69·6 g ; 0·2 mole), or trichlorotitanium mono-*n*-butoxide (tripyridinate 93·0 g ; 0·2 mole) in boiling hexane (400 ml) was treated dropwise with dry butanol (29·6 g ; 0·4 mole) (or excess) over a period of 1 hr. After refluxing for a further 3 hr, the insoluble material was removed by filtration and the filtrate concentrated under vacuum. Fractionation gave titanium tetra-*n*-butoxide, b.p. 172 °C/3 mm, $n_D^{20}=1·4398$. in a yield of 35%.

(v) *Exchange Reactions.*—Trichlorotitanium mono-*n*-butoxide tripyridinate (46·5 g ; 0·1 mole) suspended in cooled dry hexane (200 ml) was treated with dry ammonia gas for 8 hr. The yellow, hexane-insoluble, powder was filtered in the absence of air, washed and dried, to give a 97% yield of trichlorotitanium mono-*n*-butoxide penta-ammoniate. Similarly, titanium tetrachloride dipyridinate was treated with ammonia gas to give a 94% yield of titanium tetrachloride hexa-ammoniate.

IV. Acknowledgment

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V. References

Andrew, Yu. H., and Nikolskii, V. A. (1953).—*Sborn. Stat. Obshch. Khim.* **2** : 1428.

Cullinane, N. M., Chard, S. J., Price, G. F., and Millward, B. B. (1952).—*J. Appl. Chem.* **2** : 250.

Dunn, P. (1959).—*Aust. J. Appl. Sci.* **10** : 458.

Fowles, G. W. A., and Pollard, F. H. (1953).—*J. Chem. Soc.* **1953** : 2588.

Piper, T. S., and Rochow, E. G. (1954).—*J. Amer. Chem. Soc.* **76** : 4318.

Rosenheim, A., and Schutte, O. (1901).—*Z. anorg. Chem.* **26** : 245.

Trost, W. R. (1951).—*Canad. J. Chem.* **29** : 877.

APPENDIX 6 ORGANOTIN COMPOUNDS - INITIAL SURVEYS

6a	Xerox copy of original minute on Organotin Polymers	6.2
6b	Organotin Polymers - August, 1958	6.3 - 6.12
6c	Organotin Polymers - October, 1958	6.13 - 6.19

The work presented at Appendices 6b and 6c is a retype from original documents. Minor editing has been undertaken in order to conform to the general style of the thesis. The format, references and system of units originally used have not been changed.

APPENDIX 6a

DEFENCE STANDARDS LABORATORIES

MINUTE PAPER

Head, General Chemistry Group. Date 29/8/58.

ITION OF Mr. Hall.

S TO

Your ref. Our ref.

SUBJECT:

Organo-tin polymers.

Please find attached a report on organo-tin polymers, and suggestions for the preparation of possible new types of interest to us.

P Owen

Mr Standish

These proposals of P.O.'s are very interesting & of course well worth examination. We cannot pursue this line of work under existing circumstances; he must have an E.O. assistant to handle the more mundane matters on plastics. I propose therefore to transfer Kelso to work under P.O. at the earliest convenient opportunity but this would not be before the end of September as the schedule of tests Boyd & Kelso have in progress will probably not be finished before then.

19

APPENDIX 6b

DEFENCE STANDARDS LABORATORIES

MINUTE PAPER

TO Head, General Chemistry Group

Date 29/8/58

ATTENTION OF Mr. Hall

Your ref. *Our ref.*

COPIES TO

SUBJECT:

Organotin polymers

Please find attached a report on organotin polymers, and suggestions for the preparation of possible new types of interest to us.

(Signed) P. DUNN

ORGANOTIN POLYMERS

1. INTRODUCTION

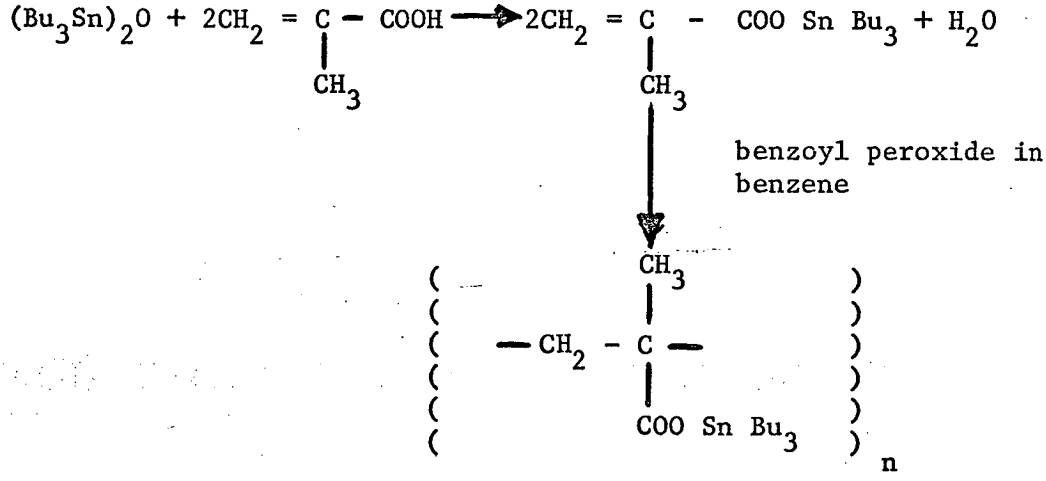
The need for new plastics, rubbers and adhesives to withstand the increasing operating temperatures of modern Service equipment, has prompted considerable research activity on new types of polymeric materials during the last few years. Organopolymers based on metals such as silicon, titanium, phosphorus, aluminium, molybdenum and boron have recently assumed considerable importance.

2. ORGANOTIN POLYMERS

The interesting properties of some organotin compounds indicate that organotin polymers might have special properties worthy of investigation. Following suggestions to certain senior staff members during 1957 that organotin methacrylic esters should produce polymeric materials, it is interesting to note that American workers (1) have recently published research papers on new rubberlike compounds based on methacrylic acid. The Quartermaster Corps, US Department of the Army is investigating the use of organometallic compounds for high temperature fire-retardant elastomers (Project No. 7-93-15-004). A recent report on this project states (2):-

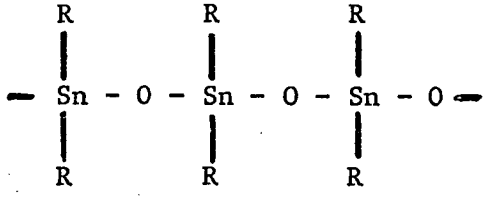
"Various organic salts of tin have been synthesized and polymerization studies of these compounds are being conducted. Preliminary results show that tin derivatives of succinic, adipic, sebacic and acrylic acids polymerize to rubbery materials. Other metals at present under consideration include zirconium, boron, phosphorus and titanium."

The organotin elastomers reported by Montermoso et al (1) are chain-type vinyl compounds with typical rubberlike properties. The polymers vary from viscous oils to tough rubbers. They are prepared as follows:-



Polymers made from acrylic acid in a similar manner are softer and less tough than those derived from methacrylic acid. The polymerization can also be carried out in a water emulsion at 50°C using a non-ionic emulsifying agent and the lauryl mercaptan-potassium persulphate system as modifier-catalyst.

Dialkyl and diaryltin oxide polymers $(R_2SnO)_n$ are insoluble and infusible materials. The carboxylic acid and alkoxy derivatives are similar to silicon and carbon compounds. Brydson (3) has discussed linear polystannoxanes of the type :-



, and some of these materials are covered by patent applications (4,5).

Polymeric compounds derived from dialkyl dialkoxytin have been reported by Mack and Parker (6). These materials are used as stabilizers for poly(vinyl chloride) compositions.

Esters of inorganic acids of aluminium, titanium and tin, and their polymers have been reported by Rothrock (7). Interpolymers of tetramethyl allyl tin and methyl methacrylate can be made and are reported to be white, enamel-like materials resistant to wear. Langkammerer (8) has polymerized tin esters of α-β unsaturated acids. Tin(tetramethyl methacrylate) and trimethyltin methacrylate can be polymerized either alone or in a mixture with styrene by heating in the presence of benzoyl peroxide as a catalyst. The products formed are suitable for moulding materials, film manufacture and coating compositions. Poly(tin tetra(methyl methacrylate)) in sheet form, has also been described by Marks (9). The material has an electrical resistivity of 10^6 ohm per sq cm.

An interesting type of organotin polymer has been briefly described by Yakubovich and coworkers (10). Chloromethyltin compounds are prepared from tin tetrachloride and diazomethane. If benzene is used as the solvent high molecular weight products are produced. The proposed reaction is:-

$$SnCl_4 + CH_2N_2 \text{ (benzene)} \longrightarrow (CH_2 = SnCl_2) \quad \text{(probably)}$$

$$\text{trace } H_2O \downarrow$$

$$-CH_2-Sn(Cl)(Cl)-CH_2-Sn(Cl)(Cl)-$$

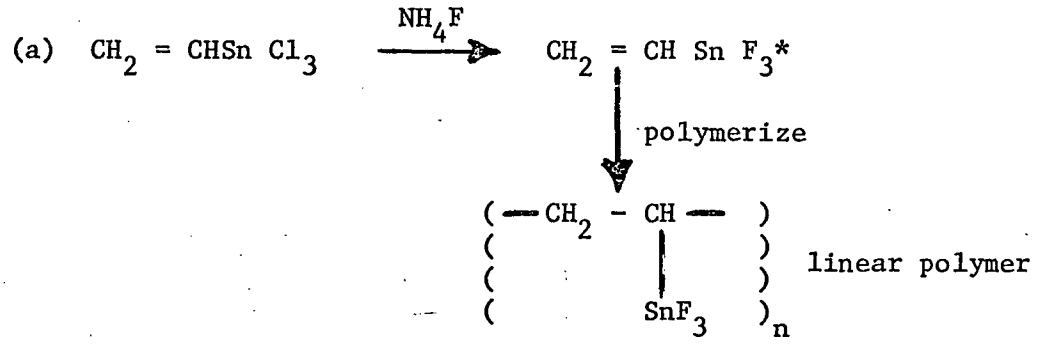
In a later paper however, the same workers (11) report that under controlled conditions the same reaction gives bis(chloromethyl)tin dichloride:-

$$SnCl_4 + 2CH_2N_2 \xrightarrow[3^o-5^oC]{\text{benzene}} (ClCH_2)_2\ Sn\ Cl_2$$

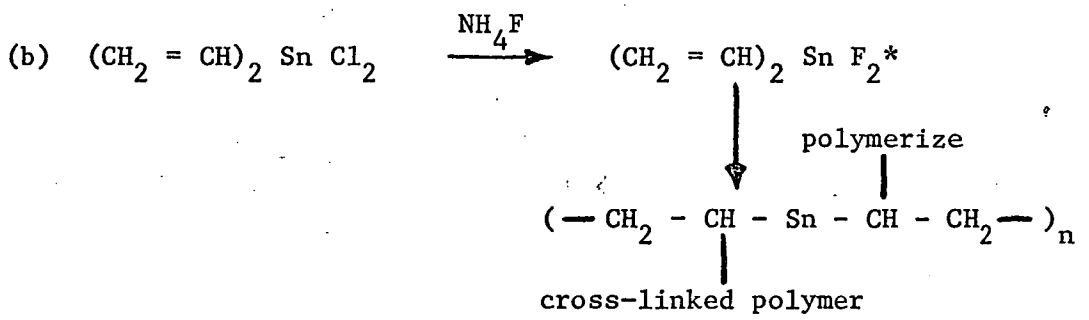
Vinyl tin monomers are now being produced in considerable quantities in the United States and a recent review by Gloskey (12) discusses the chemistry of these materials. The interest in the vinyl tins is high since there is evidence that they can be used as a nucleus for the formation of extended polymers. Practical implications are the possibility of more heat-resistance plastics as well as structurally improved plastics by cross-linking. The tetravinyltin compounds are prepared by the Grignard reaction, from vinyl magnesium bromide and stannic chloride, using tetrahydrofuran as the solvent (13). The mono - , di - , and tri-substituted vinyl compounds are prepared from the tetra substituted compound by disproportionation with stannic chloride.

3. ORGANOTIN HALIDES

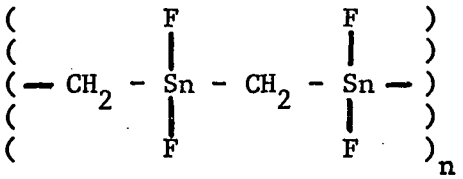
Considering the current interest in organic fluorine compounds it is hard to understand why so little work has been reported on organotin fluorides. Replacing chlorine by fluorine in a tin compound, markedly improves its thermal stability. (Triphenyltin chloride has a mp of 107°C while the corresponding fluoro compound decomposes at 360°C.) This observation immediately suggests that polymers derived from organotin fluorides could have good heat-resistant properties. Two possible vinyl type polymers are:-



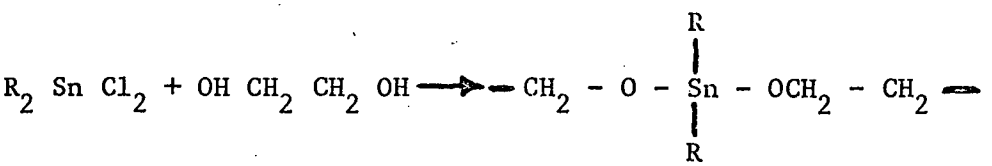
* Indicates a new compound (monomer).



Fluorination of the chlorine-containing polymer reported by Yakubovich and coworkers (10) should produce the linear and symmetrical material:-



Reaction of dialkyl or diaryltin dichloride with polyhydric alcohols should produce polymeric products. The aryl substituted compounds show greater thermal stability than their alkyl counterparts and would be preferred in this reaction:-

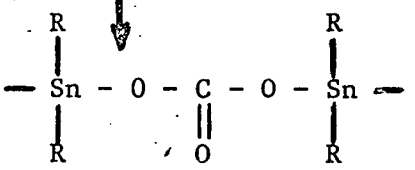


4. ORGANOTIN POLYCARBONATES

The interesting properties of the new polycarbonates (14) suggest that the tin analogues of these materials would be worthy of investigation. As dihydroxytin compounds are unstable the methyl esters would have to be used as starting materials. Two possible reactions are:-

(a) $R_2SnCl_2 + 2\ MeO\ Na \longrightarrow R_2\ Sn\ (O\ Me)_2$ --- (a)

$\downarrow$ $COCl_2$ under heat and pressure

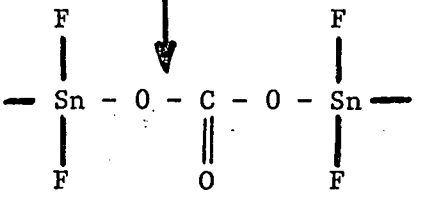


polyorganotin carbonate

(For R = ethyl or phenyl in (a) see Ref (15)).

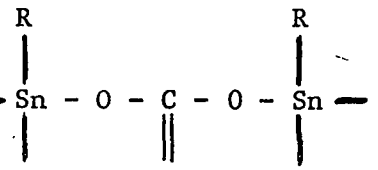
(b) $(RO)_2\ Sn\ Cl_2 \xrightarrow{NH_4F} (RO)_2\ Sn\ F_2$*

$\downarrow$ $COCl_2$ under heat and pressure



polydifluorotin carbonate

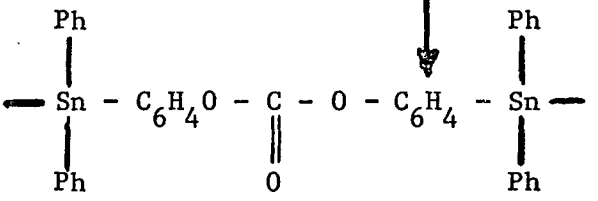
The reaction between chlorotin compounds and ammonium carbonate to form an organotin carbonate may also warrant investigation, namely:

$R_2\ Sn\ Cl_2 + (NH_4)_2\ CO_3 \longrightarrow$  $+ 2NH_4\ Cl$

Hydroxy-substituted alkyl or aryl groups in tin compounds should also react with phosgene or diphenyl carbonate to form organotin carbonate. The following reactions are proposed:-

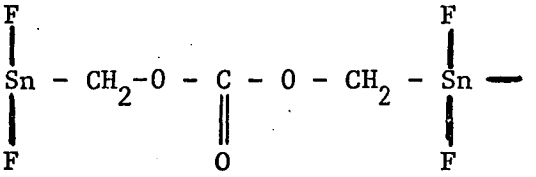
(a) $Br\ C_6H_4\ OH(4) + Bu\ Li + Ph_2\ Sn\ Cl_2 \xrightarrow{Mg\ Br_2} Ph_2Sn(C_6H_4OH)_2$ (I)

$\xrightarrow{CO\ Cl_2}$

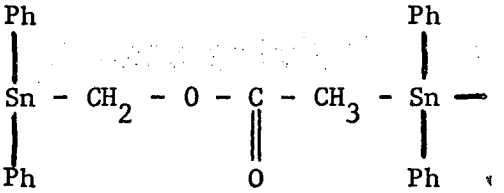


Compound (I) has been reported by Gilman and Arntzen (16) and Arntzen (17).

(b) $(HO\ CH_2)_2\ Sn\ F_2{}^* + CO\ Cl_2 \longrightarrow$



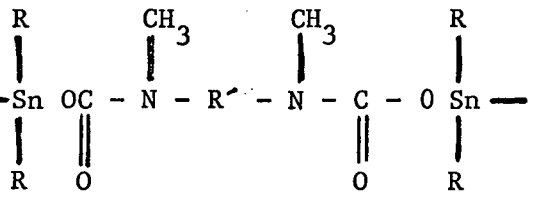
(c) $(HOCH_2)_2\ Sn\ Ph_2{}^* + CO\ Cl_2 \longrightarrow$



5. ORGANOTIN POLYURETHANES

Tin containing polymers analogous to the polyurethanes may also be prepared as follows:-

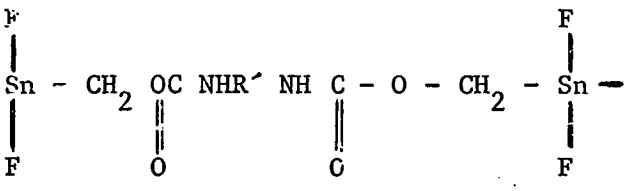
(a) $R_2\ Sn\ (OMe)_2 + R'(NCO)_2 \longrightarrow$



Organosilicon urethanes have recently been prepared by a similar method (18).

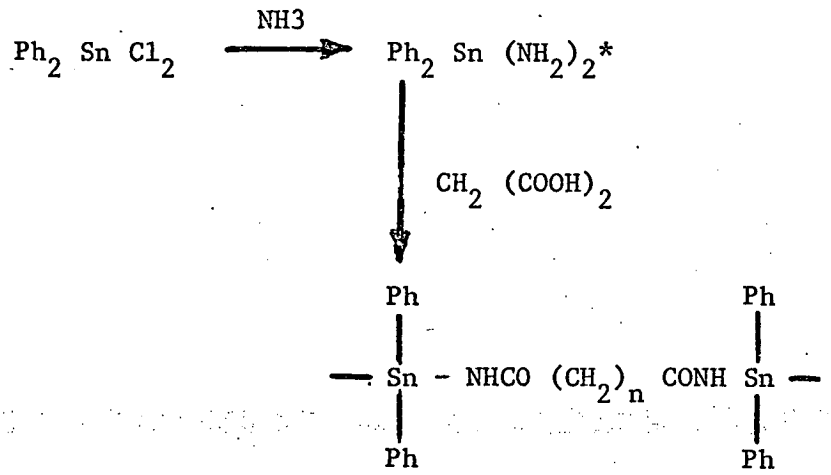
(b) $(((4)\ NH_2\ C_6H_4)_2)^*\ Sn\ F_2 \xrightarrow{CO\ Cl_2} ((4)\ NCO\ C_6H_4)_2\ Sn\ F_2{}^*$

$\downarrow$ React with -OH compound to form urethane polymer.

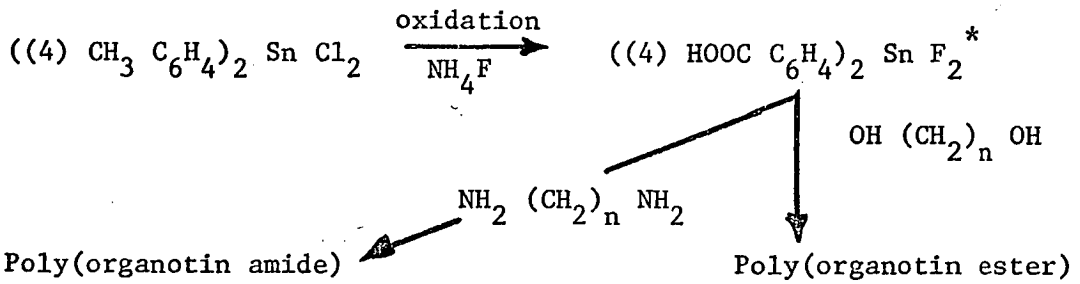
(c) $F_2\ Sn\ (CH_2OH)_2$* + R´ $(NCO)_2$ ⟶ 

6. ORGANOTIN POLYAMIDES

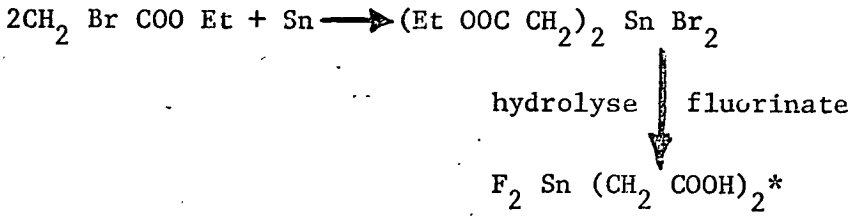
The synthesis of diaminodiphenyltin would enable the preparation of polyamide type polymers according to the scheme:-



Organotin compounds containing an azo linkage have been described by Gilman and Rosenberg (22). Kocheshkov and coworkers (19) have prepared p-methyl phenyltin chlorides by disproportionation from tetra(p-methyl phenyl)tin. Oxidation of this material by chromic acid or permanganate should give a carboxylic acid derivative, which could be used for the preparation of polyamide or polyester tin compounds :-



The preparation of aryl carboxylic esters of tin has also been described by Eskin (20). In this reaction,metal interchange with the corresponding mercury compound is used :-



This material could be used as a starting material for polyester or polyamide type resins.

Alkyl substituted tin compounds have been prepared by Jones (23) and Vijayraghaven (24) by the Grignard reaction from alkyl magnesium bromide. There are no reports that these materials have been polymerized. On the other hand diallyloxy dibutyltin has been prepared and polymerized by Mack and Parker (15). These materials when dissolved in an ester or hydrocarbon solvent can be used in resin formulations.

7. CONCLUSIONS

Reports in the literature indicate that organotin polymers are receiving considerable attention overseas in view of their possible usage as heat-resistant elastomers. The vinyl type polymers appear to be the most promising. However it should be possible to prepare many other types of organotin polymeric materials and some chemical reactions for these have been proposed.

(Signed): P. DUNN
26/8/58

General Chemistry Group,
Materials and Explosives Division.

8. REFERENCES

1. Montermoso et al., Chem and Eng News. 36, No. 16, 50 (1958)

2. US Department of the Army, (Quartermaster Corps), Consolidated Research and Development, Annual Project Report, Vol. 1. p317 (1957)

3. Brydson, Plastics 22, 384, (1957)

4. Du Pont, U.S.P. 2, 484, 508

5. Advance Solvents and Chemical Co., U.S.P. 2, 628, 211

6. Mack and Parker, U.S.P. 2, 626, 953 (1953) (Chem. Abs. 47, 11224(c), (1953))

7. Rothrock, U.S.P. 2, 258, 718 (1942) (Chem. Abs. 36, 595 (1942))

8. Langkammerer, U.S.P. 2, 253, 128 (1948) (Chem. Abs. 35, 8151 (1941))

9. Marks, U.S.P. 2, 687, 395 (1954)

10. Yakubovich et al., Chem. Abs. 45, 2857(b) (1951)

11. Yakubovich et al., Chem. Abs. 47, 9257(b) (1953)

12. Gloskey, Ind Eng Chem., 49, No. 12, 47A (1957)

13. Seyferth and Stone, J. Amer. Chem. Soc. 79, 515 (1957)

14. Thompson and Goldblum, Mod. Plast. 35, No. 8, 131 (1958)

15. Mack and Parker, U.S.P. 2, 700, 675 (1955) (Chem. Abs. 50, 397(h) (1956))

16. Gilman and Arntzen, J. Org. Chem. 15, 994 (1950)
(See also Chem. Abs. 50, 10670(b) (1950))
(Chem. Abs. 38, 61 (4) (1944)).

17. Arntzen, Iowa State College, J. Sci. 18, 6 (1943)

18. Astakhin, Losev and Andrianov, Doklady Akademii Nauk. S.S.S.R. 113, No. 3, 581 (1957)

19. Kocheshkov et al., Chem. Abs. 28, 7253 (6) (1934)
Chem. Abs. 28, 4711 (4) (1934)

20. Eskin et al., Chem. Abs. 32, 5386 (8) (1938)

21. Gilman and Leeper, J. Org. Chem. 16, 466 (1951)
(See also Chem. Abs. 38, 727 (1944))

22. Gilman and Rosenberg, J. Amer. Chem. Soc. 74, 5580 (1952)

23. Jones et al., J. Chem. Soc. 1446 (1947)

24. Vijayraghaven, J. Ind. Chem. Soc. 22, 119 (1945)

9. ADDENDUM TO ORGANOTIN POLYMERS

Professor van der Kerk recently described a new method for the preparation of functionally substituted organotin compounds and the polymerization of these into polymeric materials. The information is reported in the Summer, 1958 issue of "Tin and its Uses" - No. 43 p.17.

Compounds with functionally substituted groups attached to tin can be prepared by condensing a substituted tin hydride with a compound terminating in an olefinic double bond. Transference of the hydride hydrogen to the second carbon of the unsaturated pair occurs smoothly at moderate temperatures:-

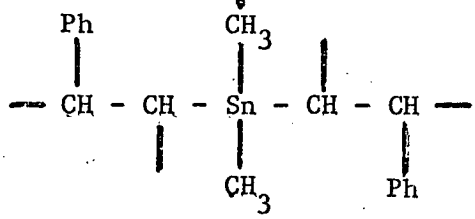
$$R_2SnH_2 + 2CH_2 = CH\ COOH \longrightarrow R_2Sn\ (CH_2CH_2\ COOH)_2$$

The mono-, di- and tripropyltin substituted compounds have been prepared by this method. The sodium salts are water soluble.

The hydride-olefin synthesis can lead to polymeric materials. The following reactions have been investigated:-

(a) $(CH_3)_2\ SnH_2 + 2Ph\ C \equiv CH \longrightarrow (CH_3)_2\ Sn(CH = CH\ Ph)_2$

phenylacetylene — polymerization



(b) $(CH_3)_2\ SnH_2 + (CH_2 = CH\ C_6H_4\ CH = CH_2)_2 \longrightarrow (CH_3)_2\ Sn(CH_2CH_2C_6H_4CH = CH_2)_2$

p-divinyl benzene — polymerization

crosslinked organotin polymer

The above reactions offer considerable possibilities for the preparation of organotin polymers.

APPENDIX 6c

DEFENCE STANDARDS LABORATORIES

MINUTE PAPER

TO Superintendent,
Materials and Explosives Division.

Date 22/10/58

FROM A/Head, General Chemistry Group.

Your ref. *Our ref.*

COPIES TO

SUBJECT:

Organotin polymers

Following a recent discussion regarding possible lines of research in the field of polymer chemistry, the attached report on "Organotin polymers" has been prepared.

In the UK, considerable effort is being made on the development of new materials for service equipment and polymers containing elements such as Si, P, B and Al, are receiving attention. Organotin materials also warrant investigation. As a specific example mention may be made of optically clear plastics materials for canopies for high speed aircraft. The present material poly(methyl methacrylate) is not entirely satisfactory and a replacement material to operate at a skin temperature of 150° - 200°C is needed. Polymers derived from tin may provide such a material.

As with most research in the field of organic chemistry it is difficult to predict what properties a particular compound might possess without first preparing the compound or some of its intermediates. The problem thus appears to synthesize some organotin polymer and investigate its properties with the view to it having some application in specialized service equipment.

(Signed): P. DUNN

ORGANOTIN POLYMERS

1. INTRODUCTION

A comprehensive review of new information in the field of synthesis of semi-inorganic polymers has recently been published by Andrianov (1) and an English translation by Lachman is available (2). The paper contains a reasoned detailed review of recent achievements in the field of semi-inorganic polymers, viz. organosilicon polymers, polyorganometallosiloxanes (including polyorganostannosiloxanes) and organophosphorus, organoboron and organobismuth polymers.

Andrianov and co-workers (3) reported that vitreous polyorganostannosiloxanes were obtained by the cohydrolysis of diethyldichlorotin with diethyldichlorosilane or dimethyldichlorosilane, or with a mixture of diethyldichlorosilane and phenyltrichlorosilane, with subsequent condensation of the products of cohydrolysis. The polyorganostannosiloxanes are formed according to the scheme:-

$$m\,R_2Si\,Cl_2 + n(C_2H_5)_2SnCl_2 \xrightarrow[NH_3]{H_2O} (-O\,Si(R)_2-)_m\,(-O\text{-}Sn(C_2H_5)_2\text{-}O-)_n$$

where m, varies from 4 to 11.

The cohydrolysis was brought about by a 10% aqueous solution of ammonia in the presence of toluene, at 50-55°C. The transparent, liquid, yellow polymers obtained were soluble in benzene, toluene, ether, acetone and alcohol. Liquid products of the hydrolysis are condensed at 105° - 150°C to transform them into solid polymers. These are non-fusible vitreous substances, insoluble in organic solvents.

Henglein and co-workers (4) describe the condensation of dimethyldiethoxy silane with diacetoxytin and with diisobutyldiacetoxytin. The reactions are:-

(a) $$n\,(CH_3)_2\,Si(OC_2H_5)_2 + n\,(CH_3)_2\,Sn\,(O\,COCH_3)_2 \longrightarrow$$

$$\longrightarrow (-Si(CH_3)_2 - O - Sn(CH_3)_2 - O-)_n + 2nCH_3\,CO\,O\,C_2H_5$$

(b) $n\,(CH_3)_2\,Si\,(OC_2H_5)_2 + nR_2Sn(O\,COCH_3)_2 \longrightarrow$

$$\longrightarrow C_2H_5O\left(-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Sn}}-O\right)_n - OCOCH_3 + 2nCH_3\,COO\,C_2H_5$$

where R is, iso - C_4H_9.

Besides the reaction trend which results in polymer formation, another reaction takes place that gives products of high molecular weight. The crystalline dimer, sym(diacetoxy tetraisobutyl)distannoxane, has been isolated namely:-

$CH_3COOSn\,(i\text{-}Bu)_2\,\text{-}O\text{-}O\,(i\text{-}Bu)_2\,Sn\,O\,COCH3.$

Alkyltin acetates have been described by van der Kerk and Luijten (5), and others (6,7).

2. TOXICITY OF ORGANOTIN COMPOUNDS

The hazards involved in handling organotin compounds have recently received considerable attention, and a general review by Lyle (8), discusses lesions of the skin in process workers caused by contact with butyltin compounds. The toxicity of the tin compounds varies with structure, molecular weight and solubility. Most tin compounds are harmless because of insolubility in body fluids. However some alkyl derivatives are soluble and very toxic. Diethyl and triethyltins are the most toxic, while the corresponding octyl compounds are claimed by Luijten and Pezarra (9), to be non toxic. No evidence of any general toxic effects arising from absorption of butyltin compounds has been found among workmen concerned in the processing of these compounds. Care, however should be taken to prevent skin contact with alkyltin derivatives.

3. ORGANOTIN ANTIOXIDANTS

The use of organotin compounds as non-staining, non-discolouring antioxidants for vulcanized natural and synthetic rubbers has recently been announced in the United States (10, 11, 12). The compounds are of the type, $R_nSn\,(OR')_{4-n}$ where R is alkyl, aryl or aralkyl, OR' is mono or dihydric aliphatic alcohol or phenol, and n is 1, 2 or 3. Polymeric tin compounds are also claimed to have antioxidant properties. Thus materials of the type,

$$R_2SnCl\left(-O\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Sn}}-\right)_n Cl,$$

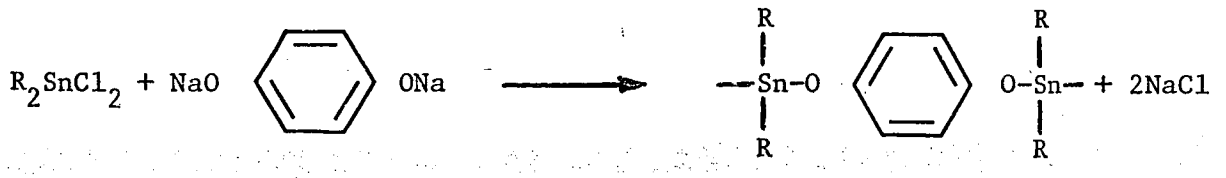
where R is alkyl, aryl or aralkyl and n is up to 20, have been prepared and tested.

4. ORGANOTIN FLUORIDES

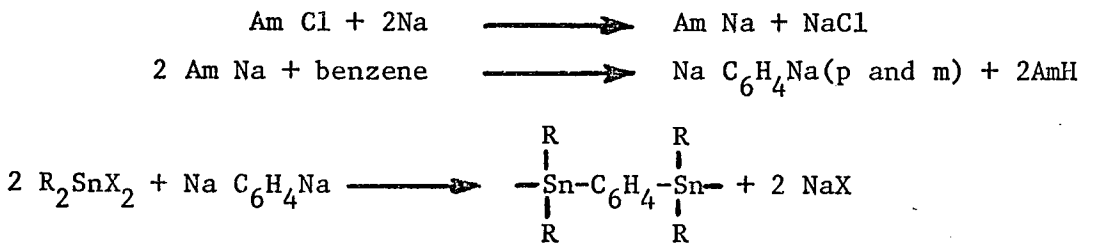
Krause and Becker (13) have prepared di- and triaryltin fluorides by the action of aqueous hydrofluoric acid on the corresponding bromo compounds. The aryltin fluorides are high melting, white solids. The di- and trialkyltin fluorides have also been prepared by similar methods by Krause (14). An elegant method for the preparation of aryl- and alkyl-tin fluorides is the fluorination of the appropriate chloro compounds with anhydrous ammonium fluoride. (Note added 1978: Records show that triethyltin fluoride, tributyltin fluoride and triphenyltin fluoride were prepared at DSL during 1958. A laboratory report on the toxicity of these fluorides and on tributyltin acetate and triphenyltin acetate was issued at DSL on 11 August, 1958. Details are given in Section 5.7 and Appendix 7).

5. NEW ORGANOTIN POLYMERS

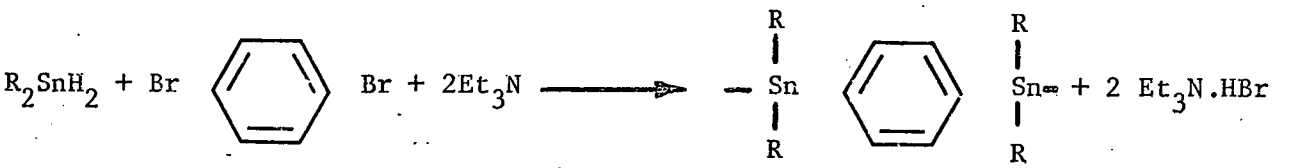
The reaction between dialkyltin dichloride and the disodium salt of hydroquinone may also lead to polymeric products, such as:



Similarly the reactivity of certain bimetal benzene compounds may lead to the formation of Sn - C bonds and long chain compounds. Disodium benzene has been prepared by the reaction of n-amyl sodium on benzene (15). This compound may then react with dichloro- or dibromodialkyltin compounds in the following manner:-



Investigation of the reaction between dihalobenzene and dialkyl or diaryltin dihydrides may also be warranted. Many organotin hydrides have been prepared by van der Kerk, Noltes and Luijten (16), and by Dillard and coworkers (17), by the reduction of the appropriate organotin chloro compound with lithium aluminium hydride. The following reaction is suggested:-



where R is methyl, ethyl or phenyl. A polymer formed in the above reaction where R = CH_3 should be thermally very stable.

The literature contains very few references to halogen - containing ortho esters of tin. Meerwein and Bersin (18) and Thiessen and Koerner (19) have reported that use of excess alcohol in the sodium ethoxide reaction gives an addition complex of the tetraethoxide. A possible route to the dialkoxytin dichlorides may be through the disproportionation reaction between stannic chloride and tin tetraalkoxide, viz:

$$(RO)_4Sn + SnCl_4 \longrightarrow 2\ (RO)_2SnCl_2$$

Rosenheim and Schnabel (20) and Schwartz and Reinhardt (21) both describe the vigorous reaction between primary alcohols and stannic chloride. The hydrochloric acid liberated during the reaction forms an addition complex with the partially esterified tin compound:

$$2\ ROH + Sn\ Cl_4 \longrightarrow (RO)_2Sn\ Cl_2 .\ HCl + HCl$$

Use of sodium alkoxide in the above reaction should eliminate the possibility of addition complex formation:

$$2\ RONa + Sn\ Cl_4 \xrightarrow{\text{toluene}} (RO)_2\ Sn\ Cl_2 + 2\ NaCl$$

As the fluoro compound would be more stable than the chlorocompound, fluorination of the crude reaction mixture with ammonium fluoride before final purification may be advisable.

Recently Andrews and coworkers (22) have described the preparation of a number of dibutyltin dicarboxylic acid esters which are potentially useful in the synthesis of organotin elastomers. Dibutyltin oxide and dibutyltin diacetate were found to react readily with linear and cyclic dicarboxylic acids and anhydrides to form identical derivatives. The cyclic terphthalic and long chain sebacic acids give linear polymers, with molecular weights varying from that of the dimers to the order of 3000 for the sebacic acid product. The general type of reaction is illustrated by the reaction of dibutyltin diacetate and a dicarboxylic acid:

$$n\ Bu_2Sn(OAc)_2 + n\ HOOCR_x\ COOH \longrightarrow -\underset{\displaystyle Bu}{\overset{\displaystyle Bu}{\overset{|}{\underset{|}{Sn}}}}-O\ COR_xCO\ O-\underset{\displaystyle Bu}{\overset{\displaystyle Bu}{\overset{|}{\underset{|}{Sn}}}}- + 2nAcOH$$

The R group may be short or long chain with methylene groups, with or without substituted groups, a ring compound or combination of these.

6. GENERAL

Polymers which contain inorganic elements in molecular chains form a group of substances which are the first examples from the little known boundary region between organic polymers and inorganic substances such as quartz, silicates, carborundum, polytitanates, etc. The inorganic chains of the molecules of these polymers render them similar to inorganic substances, while the "framing" carbon-containing groups relate these polymers to the well known organic high polymers. It is necessary to produce new polymers which should reduce the wide qualitative gap in such very important properties as heat resistance, elasticity and solubility between the organic and the inorganic polymers. The organic polymers, while possessing exceptionally valuable elastic properties, lack the very desirable heat resistance, whereas inorganic polymers lack elastic properties.

Organotin compounds are at present being used for:- anticorrosion additives, plastic stabilizers, biocides and fungicides, curing catalysts for silicone elastomers, dielectric fluids and poultry medicines. In 1946, only a few hundred pounds of tin found its way into organic compounds. In 1956, the figure approached 150,000 pounds and by the end of 1960 an annual output of 2.5 million pounds of organotins is expected, chiefly butyltin compounds such as bis(tri-n-butyltin) oxide.

Organotin research may lead the way to still another and potentially tremendous area. Widespread research today in the USA and Europe, looks towards incorporating metals in polymers, either for crosslinking, or as an integral part of the substituent monomer. Some of these loosely termed "inorganic plastics" (for example, silicones) are expected to show unbelievable heat resistance and toughness.

Tin resembles silicon in some of its reactions. So tin-containing compounds akin to silicones, may well be the first of these materials commercially made. The structure of such combinations has not yet been fully determined. Hydrocarbon radicals like vinyls seem to offer especially interesting opportunities, perhaps because of their unsaturated character.

This work still in its early stages, may grow large in the next few decades. Development is being pushed on a broad front by Government laboratories, basic metal producers, petroleum refiners and manufacturers of conventional resins and plastics. Synthetic metal-containing organic compounds will most likely, according to industry leaders, be the outstanding source of new materials in the future.

It is interesting to note that research work in the Ministry of Supply, UK, and at British Universities with Ministry of Supply extra-mural research contracts, is not directed specifically towards elastomers, plastics, lubricants, etc., but towards the production of <u>any polymer</u> which may prove useful in these fields, or in any other field in which it may have a particular application.

7. REFERENCES

1. Andrianov, K.A., Uspekhi Thimii., 26, No.8, 895 (1957)

2. Lachman, F., R.A.E. Translation No. 710 (1958)

3. Andrianov, K.A., Ganina, T., and Khrustaleva, E., Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Naick. 798 (1956)

4. Henglein, F., Lang, R. and Schmack, Z., Die Makromolekulare Chemie, 22, 103 (1957)

5. van der Kerk, G.J.M., "Tin and its Uses" 43, 17 (Summer, 1958)

6. van der Kerk, G.J.M., Noltes, J.G., and Luijten, J.G.A., J. Appl. Chem. 7, 356 (1957)

7. van der Kerk, G.J.M., Noltes, J.G., and Luijten, J.G.A., J. Appl. Chem. 7, 366 (1957)

8. Lyle, W.H., Brit. J. industr. Med. 15, 193 (1958)

9. Luijten, J.G.A., and Pezarra, S., Brit. Plast. 30, No. 5,183 (1957)

10. "New World of Chemicals", Chem. and Eng. News (Special Report) 36, No. 30, 44 (1958)

11. Tomka, L.A. and Weinberg, E.L., U.S.P. 2, 798, 862. (Chem. Abs. 51, 15166, (1957))

12. Tomka, L.A. U.S.P. 2, 798, 863 (Chem. Abs. 51, 15166, (1957))

13. Krause, E. and Becker, R., Ber. 53B, 173 (1920) (Chem. Abs. 14, 2634 (1920))

14. Krause, E., Ber. 51, 1447 (1918) (Chem. Abs. 13, 726 (1919))

15. Morton, A.A. and Claff, C.E., J. Amer. Chem. Soc. 76, 4935 (1954)

16. van der Kerk, G.J.M., and Luijten, J.G.A., J. Appl. Chem. 6, 56 (1956)

17. Dillard, C.R., McNeil, E.H., Simmons, D.E. and Yeldell, J.B., J. Amer. Chem. Soc. 80, 3607 (1958)

18. Meerwein, H. and Bersin, T., Ann. 476, 113 (1929) (Chem. Abs. 24, 586, (1930))

19. Thiessen, P.A. and Koerner, O., Z. anorg. allgem. Chem. 195, 83 (1931) (Chem. Abs. 25, 1177, (1931))

20. Rosenheim, A. and Schnabel, R., Ber. 38, 2777 (1905)

21. Schwartz, R. and Reinhardt, W., Ber. 65, 1743 (1932)

22. Andrews, T.M., Bower, F.A., La Liberte, B.R. and Montermoso, J.C., J. Amer. Chem. Soc. 80, 4102 (1958)

APPENDIX 7 TOXICITY OF ORGANOTIN COMPOUNDS

7a Toxicity of Organotin Compounds 7.2

The work presented at Appendix 7a is an unabridged retype of the original laboratory report.

APPENDIX 7a

TOXICITIES OF ORGANOTIN COMPOUNDS

Toxicities were determined using rats as test animals. The organotin compounds were homogenized in propylene glycol and injected via the intraperitoneal route. In each case deaths were recorded after six (6) days (12 days for triphenyltin fluoride).

TABLE I. Toxicities of Tin Compounds

Compound	Physical constants, °C	Dose (mg/kg)	Response (deaths)	Probable MLD100 (mg/kg)
Triethyltin fluoride	mp, 179 - 180	5	0/10	
		10	9/10	
		15	7/10	5-15
		25	10/10	
Tri-n-butyltin acetate	mp, 84 - 85	14	8/10	
		21	10/10	
		28	9/10	14-21
		35	9/10	
Tri-n-butyltin fluoride	mp, 218 - 219	10	6/10	
		17	6/10	
		24	4/10	30
		30	6/10	
Triphenyltin acetate	mp, 118 - 120	20	7/10	
		27	10/10	
		34	7/10	25-30
		40	10/10	
Triphenyltin fluoride	Decomposes 360 - 365	10	0/1	
		20	0/1	
		30	1/1(10d)	
		40	0/1	30-60
		50	1/1(11d)	
		60	0/1	
		70	1/1(4d)	
		100	1/1(5d)	
		125	1/1(2d)	
		150	1/1(½h)	

Toxicities were determined by Mr. L. Austin*, Physiology Group, DSL.

(Signed): P. DUNN 11/8/58

* Note added 1978. Now Dr L. Austin, Reader, Department of Biochemistry, Faculty of Medicine, Monash University, Clayton, Victoria.

APPENDIX 8 ELASTOMERIC AND FUNGICIDAL ORGANOTIN COMPOUNDS

8a Elastomeric and Fungicidal Organotin Compounds.
P. DUNN. Paper presented at ANZAAS*, Sydney, August 1962. 8.2 - 8.19

8b Organotin Compounds as Fungicides for Natural and Synthetic Rubbers.
P. DUNN 8.20 - 8.26

8c Copolymers of Tributyltin Methacrylate and Chloroethyl Vinyl Ether.
P. DUNN 8.27 - 8.30

The work presented at Appendix 8a is an unabridged retype of the manuscript of the paper presented at ANZAAS. The work presented in Appendices 8b and 8c is a retype from original laboratory documents, with minor editing.

* ANZAAS: Australian and New Zealand Association for the Advancement of Science. A history of ANZAAS is reported in *Aust. J. Sci.*, 25, No. 4, 2 (1962-63).

The thirty-sixth Congress of ANZAAS, held mainly at the University of Sydney, 20-24 August 1962, was observed as a Jubilee marking 75 years of the Association's activity. Details of the Congress have been reported by Elkin, A.P. 1962-63. *Aust. J. Sci.*, 25, No. 4, 123.

In addition to the paper listed at Appendix 8a, a paper entitled *The Infrared Spectra of Organotin Compounds* by R.A. Cummins and P. Dunn, was also presented at ANZAAS, 1962. Details of the published version of this latter paper are given at Appendix 10a (p. 10.2).

APPENDIX 8a

Paper presented at ANZAAS Sydney, August, 1962

ELASTOMERIC AND FUNGICIDAL ORGANOTIN COMPOUNDS

by P. DUNN *

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Summary

In recent years the elastomeric and fungicidal properties of organotin compounds have been of considerable interest.

This paper discusses the use of both emulsion polymerization techniques and organic peroxides to prepare polymeric materials based on tributyltin methacrylate and acrylate. Copolymers of organotin esters with unsaturated monomers such as styrene, methyl methacrylate and butyl methacrylate are also described. Attempts have been made to crosslink these polymers to obtain materials resistant to high temperatures and oils.

Trialkyltin compounds are powerful biocidal agents and experiments to evaluate these compounds as fungicides for plastics and rubbers are described. Tributyltin methacrylate or acrylate may be compounded into a plastics or rubber mix and then polymerised in-situ during subsequent processing.

The preparation of a series of trialkyltin compounds containing different functional groups, and the effect of these groups on the fungicidal properties of the materials, is described. The methods of evaluation are discussed.

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ELASTOMERIC AND FUNGICIDAL ORGANOTIN COMPOUNDS

1. INTRODUCTION

The need for new plastics, rubbers and adhesives to withstand the increasing operating temperatures of modern service equipment, has prompted considerable research activity on new types of polymeric materials during the last few years. Organometallic polymers based on metals such as silicon, titanium, phosphorus, aluminium, molybdenum and boron have, in this regard, received considerable attention.

Polymers which contain inorganic elements in the basic structure lie in the region between the true organic polymers, such as polyethylene on the one hand, and inorganic substances such as quartz and silicates on the other. The organic polymers possess valuable elastic properties but generally have poor heat resistance, while the inorganic polymers have good heat resistance but lack elastic properties. The organometallic polymers of current interest might lie midway between the organic and inorganic polymers in such properties as heat resistance, elasticity and solubility.

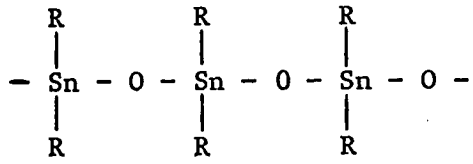
Of the many organometallic compounds known, only the silicones have achieved wide industrial acceptance. However, other Group IV elements of the Periodic Table react similarly to silicon and carbon and, of these, tin could form compounds that might lead to polymers with interesting properties.

2. ORGANOTIN POLYMERS

Organotin compounds are at present being used for anti-corrosion additives, plastics stabilizers, biocides and fungicides, curing catalysts for silicone elastomers, dielectric fluids, and poultry medicines. In 1946, only a few hundred pounds of tin found its way into organic compounds. In 1956 the figure approached 150,000 pounds and by the end of 1960 the annual output was 2.5 million pounds of organotins, chiefly butyltin compounds such as bis(tri-n-butyltin) oxide.

It is important, at this stage, to mention the active interest of scientists overseas in the chemistry of organometallic compounds. In both America and Russia research and development on a wide variety of organometallic compounds is being actively carried out. In this regard a comprehensive review of new information in the field of synthesis of semi-organic polymers has recently been published by Andrianov (1) and an English translation by Lachman is available (2). This review describes certain organotin polymers, and indicates the activity of Russian chemists in the field of organometallic compounds.

Dialkyl and diaryltin oxides exist as polymers $(R_2SnO)_n$, and are insoluble and infusible materials while the carboxylic acid and alkoxy derivatives are similar to silicon and carbon compounds. Brydson (3) has discussed linear polystannoxanes of the type:-



and some of these materials are covered by patent applications. As well as linear polystannoxanes, cyclic polymeric compounds can also be formed, and the structures of these polymers are given in Figure 1.

Adrianov and co-workers (4) reported that vitreous polyorganostannesiloxanes were obtained by the cohydrolysis of diethyldichlorotin with diethyldichlorosilane or dimethyldichlorosilane, or with a mixture of diethyldichlorosilane, and phenyltrichlorosilane, with subsequent condensation of the products of co-hydrolysis (Figure 1). Similar stannosiloxanes have also been reported by Koenig (5), who claims the polymers have a molecular weight range of 1000-5000 and an order of thermal stability comparable to that of poly(diphenyl siloxane).

Polymeric compounds derived from dialkyldialkoxytin have been reported by Mack and Parker (6), and these materials are used as stabilizers for poly(vinyl chloride) compositions. Esters of inorganic acids of aluminium, titanium and tin and their polymers have also been reported by Rothrock (7). Interpolymers of tetra(methyl allyl)tin and methyl methacrylate can be made and are reported to be white enamel-like materials resistant to wear.

Langkammerer (8) has prepared tin esters of unsaturated acids such as tin tetra(methyl methacrylate) and trimethyltin methacrylate and shown these can be polymerized either alone or in a mixture with styrene by heating in the presence of benzoyl peroxide as a catalyst. The products formed are suitable for moulding materials, film manufacture and coatings. Poly(tin tetra(methyl methacrylate)) in sheet form, has also been described by Marks (9).

Vinyltin monomers are now being produced in considerable quantities in the United States and a recent review by Gloskey (10) discusses the chemistry of these materials. The interest in the vinyltins is high since there is evidence that they can be used as a nucleus for the formation of extended polymers.

Another type of organotin polymer described by Korshak et al (11) is poly(p-triethylstannyl α-methylstyrene). This product is obtained by polymerization at 6000 atmospheres using benzoyl peroxide as the catalyst.

3. POLYMERS WITH ELASTOMERIC PROPERTIES

Recently Andrews and coworkers (12) have described the preparation of a number of dibutyltin dicarboxylic acid esters which are potentially useful in the synthesis of organotin elastomers. Dibutyltin oxide and dibutyltin diacetate were found to react readily with linear and cyclic dicarboxylic acids and anhydrides to form identical derivatives. The cyclic terphthalic and long chain sebacic acids gave linear polymers, with molecular weights varying from that of the dimers to the order of 3000 for the sebacic acid product.

Within the last few months another novel organotin polymer has been described by Noltes and van der Kerk (13). Linear organotin polymers with molecular weights in the range 45000 to 100,000 have been prepared by polyaddition reactions involving organotin dihydrides and α-ω diynes such as 1,5 hexadiyne, namely:-

$$R_2SnH_2 + HC \equiv CR^1C \equiv CH \longrightarrow HSnR_2CH = CHR^1C \equiv CH$$

$$\downarrow$$

$$- SnR_2CH = CHR^1 CH = CH - SnR_2 -$$

These polymers range from rubberlike elastic solids to viscous oils depending on the groups R and R^1. It is interesting to note that the hexadienyltin polymers show some structural resemblance to natural rubber. Apart from the presence of methyl groups, every second $-CH_2CH_2-$ group in natural rubber has been replaced by a dialkyl or diaryltin group.

$$- CH_2 - CH = CH\ Sn\ R_2CH = CH\ CH_2 -$$

Organotin polymer

$$- CH_2\overset{CH_3}{\overset{|}{C}} = CH\ CH_2CH_2\overset{CH_3}{\overset{|}{C}} = CH\ CH_2 -$$

Natural rubber

As these polymers have residual double bonds in the chain it should be possible to crosslink them into elastomeric materials.

Diolefinic compounds will also react with organotin dihydrides to form saturated high molecular weight materials.

$$R_2Sn\ H_2 + H_2C = CH\ R^1\ CH = CH_2 \longrightarrow - Sn\ R_2CH_2CH_2R^1\ CH_2CH_2Sn\ R_2 -$$

4. ORGANOTIN ACRYLATES AND METHACRYLATES

The Quartermaster Corps, Department of Army, USA is investigating the use of organometallic compounds for high temperature fire-retardant elastomers and a recent report on this project states (14):-

> "Various organic salts of tin have been synthesized and polymerization studies of these compounds are being conducted. Preliminary results show that tin derivatives of succinic, adipic, sebacic and acrylic acids polymerize to rubbery materials. Other metals at present under consideration include zirconium, boron, phosphorus and titanium."

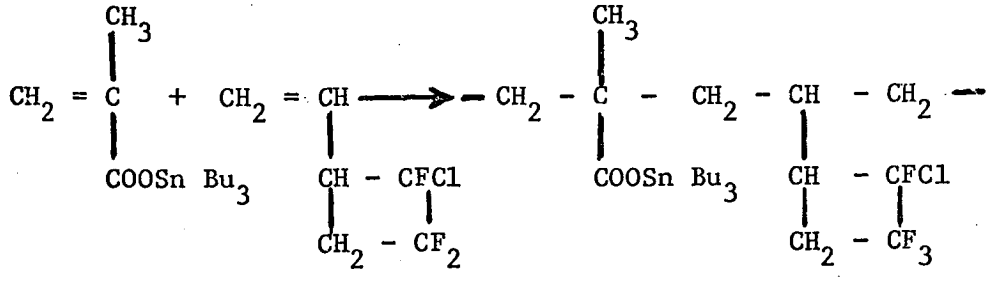
Details of this work were subsequently published by Montermoso, Andrews and Marinelli (15,16). Shostakovskii and coworkers (17) reported similar compounds, and at about the same time polymeric organotin methacrylates and acrylates were prepared at Defence Standards Laboratories. The monomers are first prepared by reacting bis(tributyltin) oxide in a 1:2 ratio with either methacrylic acid or acrylic acid. The synthesis is shown in Figure 2. The product of the reaction is a typical chain-type vinyl polymer with carbon to carbon connecting links and with the carboxyl-tin groups attached to the polymer chain.

The monomer tributyltin methacrylate appears to be very reactive, and we have prepared copolymers with acrylic acid, methyl methacrylate, butyl methacrylate, acryonitrile and styrene. These copolymers vary from hard transparent brittle solids, to thick viscous liquids.

Montermoso and his coworkers (15,16) at the Quartermaster Research and Engineering Center have also copolymerized tributyltin methacrylate with monomers such as chloroethyl vinyl phosphonate, trifluoroethyl vinyl ether and trifluoro butadiene. In each case however, polymerization was effected through the vinyl group so that the main chain consisted of carbon-carbon linkages, a structure which did not lead to high heat stability. By reacting butadiene with monochlorotrifluoro ethylene a new monomer, 1-vinyl, 2-chlorofluoro, 3-difluoro cyclobutane, b.p. 115°C, was produced.

$$CH_2 = CH - CH = CH_2 + CF_2 = CFCl \longrightarrow \begin{matrix} CH_2 - CH - CH = CH_2 \\ | \quad\quad | \\ CF_2 - CFCl \end{matrix}$$

This monomer will copolymerize with tributyltin methacrylate to form a rubberlike product, which is, at present, being evaluated by American research workers.



In the polymerization of tributyltin methacrylate using organic peroxides the reaction is similar to that which occurs during the polymerization of methyl methacrylate. Peroxide concentrations from 0.1 to 5% by weight, may be used at temperatures in the range 70°C to 150°C. Depending on conditions, the polymer can vary from a thick viscous oil to a tough rubberlike material. As the molecular weight of the polymer increases, its solubility in ether or carbon tetrachloride decreases as also does its surface tack. The polymerization with peroxides is difficult to control and reproduce, and a more consistent product may be obtained by use of emulsion polymerization techniques.

By use of a conventional lauryl mercaptan - potassium persulphate system as modifier-catalyst, a water emulsion of tributyltin methacrylate can be polymerized to a tough rubbery material. Two typical emulsion polymerization systems for tributyltin methacrylate are shown in Table 1 and the products from both reactions are similar in appearance and properties. Copolymers of tributyltin methacrylate and acrylonitrile, may also be made by the emulsion polymerization technique.

Poly(tributyltin methacrylate) is an interesting polymer but before it can be used as a material that might have commercial applications it must be crosslinked into stable elastomeric material; that is, adjacent long chains of the polymer must be joined and thus confer permanent elastic properties to the material. Although workers in America and at DSL, Australia have tried many conventional crosslinking systems with poly(tributyltin methacrylate) the results have been disappointing. Systems involving sulphur, metal oxides, phenolic resins and amines have been unsuccessful.

Some crosslinking has been obtained by American workers using dibutyltin dihydride, which shows extreme activity with allyl and vinyl groups.

Tributyltin methacrylate when polymerized by the emulsion technique is a material with a tensile strength of about 125 psi and an elongation of about 400%. When this material is crosslinked with tin dihydrides and dialkyltin oxides, rubbers with tensile strengths of about 400 psi are obtained. Typical formulations and properties are shown in Table 2.

Tributyltin methacrylate may also be copolymerized with dibutyltin dimethacrylate and the resultant polymer also can be crosslinked with dibutyltin dihydride. As shown in Table 2, the introduction of a dimethacrylate group into the polymer causes a decrease in the elongation at break and also in the volume swell figure in isooctane. As the degree of crosslinking of a particular polymer increases, the volume swell in a solvent generally decreases and this decrease can be used as a quantitative measure of the degree of crosslinking in the polymer.

5. CROSSLINKING OF ORGANOTIN POLYMERS

In our laboratories we have concentrated on trying to crosslink poly(tributyltin methacrylate) by the use of organic peroxides. As shown in Table 2 (last column), it would appear that a slight degree of crosslinking of the polymer has been obtained by the use of dicumyl peroxide, but the physical properties of these elastomers are such that, at present, they cannot be used commercially.

Dicumyl peroxide has been extensively studied as a crosslinking agent. When heated, this peroxide decomposes into free radicals which are able to remove hydrogen from certain hydrocarbons to form a polymer radical. At the same time the cumyloxy radicals formed may decompose in a second stage to form acetophenone and methyl radicals. In the vulcanization of natural rubber, 10% of the peroxide decomposed is recovered as acetophenone. The crosslinking reaction is a combination of two polymer radicals to give a carbon crosslink, and in no case does any of the peroxide combine with the polymer.

In a study of certain model systems it has been shown that dicumyl peroxide can abstract hydrogen from the active β-methylene group of n-decane, $CH_3(CH_2)_7\overset{*}{C}H_2CH_3$. In the same manner, dicumyl peroxide could act as a crosslinking agent for poly(tributyltin methacrylate) by abstracting hydrogen from the carbon atom in the β position to the carboxyl group. The reaction sequence proposed is set out in Figure 3. Experiments are being undertaken to determine the optimum conditions for any crosslinking reactions. With ethylene-propylene rubbers, the efficiency of dicumyl peroxide as a crosslinking agent can be improved by the use of sulphur, maleic acid or maleic anhydride. The mechanism of the reaction is uncertain, but in most cases the additional material becomes bound to the polymer. The enhancement of crosslinking goes through a maximum at about a molar ratio of 1:4 of sulphur to peroxide, and 2:1 of acid or anhydride to peroxide. Similar reactions occur with poly(tributyltin methacrylate) and these are being investigated. As well as dicumyl peroxide, benzoyl peroxide, ditertiary butyl peroxide, 2,4-dichlorobenzoyl peroxide, and 2,5-bis(tert-butyl peroxy)-2,5-dimethyl hexane will also induce some crosslinking in organotin methacrylates.

6. FUNGICIDAL PROPERTIES OF ORGANOTIN COMPOUNDS

One of the most interesting properties of the organotins is the biocidal activity of compounds containing trialkyl or triaryl groups. About ten years ago van der Kerk and Luijten (18) working for the Tin Research Institute, showed that trialkyl and triaryl organotin compounds were very effective against fungi, while the corresponding tetra or di- or mono-alkyl and aryl compounds were relatively ineffective. Typical results are set out in Table 3. Further these workers showed that with a particular trialkyltin compound any variation in the fourth group attached to the tin (except through the tin-carbon linkage) did not markedly affect the fungicidal activity of the compound. Table 4 shows the influence of varying Group X on the antifungal properties of compounds with the general formula $(C_2H_5)_3$ SnX.

The fungicidal activity of the trialkyl and triaryltin compounds reaches a maximum when the total number of carbons in the alkyl and aryl groups is between 9 and 15, with optimum activity for the tributyl and triisopropyltin compounds. Both these groups of compounds are about 100 times more active than the trioctyltin compounds for instance, and two to five times more active than the triphenyltin compounds.

It has been found that polymeric organotin compounds are effective fungicides for rubbers and plastics. Because these polymeric compounds are tough elastic solids they are, in this form, difficult to incorporate into some polymers, and we have found that by polymerizing tributyltin methacrylate in a solvent such as dinonyl phthalate a viscous solution of polymeric compound can be obtained that can be readily incorporated into plastics and rubbers. Polymerization can be effected by heat alone or by the use of 1% dicumyl peroxide. We have shown that a 25% solution of the polymer in plasticiser has a higher viscosity when polymerized by peroxide than when thermally polymerized. Also, on standing at room temperature, polymerization continues quite rapidly with the peroxide initiated system but only very slowly with the thermally polymerized material. Even the addition of 0.1% hydroquinone as a stabiliser does not significantly reduce the rate of polymerization of the peroxide initiated system.

Poly(tributyltin methacrylate) in solution in plasticiser, can be formulated into natural and synthetic rubbers and into plasticised poly(vinyl chloride) without difficulty. During subsequent processing such as compression moulding or extrusion, further polymerization of the tin compound takes place and the material becomes firmly bound into the finished product. In this form the tin polymers are insoluble in water and most common solvents, and thus are difficult to remove from the finished product. The results in Table 5 indicate that incorporation of four (4) parts of poly(tributyltin methacrylate) into 100 parts of polychloroprene rubber has bery little effect on the physical properties of the cured rubber. In addition, the incorporation of the organotin polymer does not enhance or impair the ozone resistance of this synthetic rubber.

We have evaluated the use of poly(tributyltin methacrylate) in rubbers and plastics using fungi obtained from the New Guinea area. The results (Table 6) indicate that in four rubbers and in poly(vinyl chloride) the incorporation of organotin polymer markedly improves the fungal resistance of the base rubber or plastics material.

Although trialkyltin compounds are very attractive fungicides, they are sensitive to ultraviolet light. When used outdoors they are gradually degraded into inactive products. Experiments at Defence Standards Laboratories indicate that to give adequate protection of a plastics or rubber for six months outdoor use, a concentration of 0.5% by weight, of the fungicide is required. Currently we are evaluating other organotin compounds in an attempt to produce materials with improved resistance to degradation by ultraviolet light.

7. CONCLUSIONS

In this paper, I hope an indication has been given regarding the interesting properties of some organotin compounds. Further work is necessary in order to crosslink polymeric tributyltin methacrylates into elastomers with useful properties. However these polymers can now be used as fungicides for rubbers and plastics which are not exposed to severe irradiation by ultraviolet light. In the future, we hope to improve the ultraviolet light resistance of these materials.

8. REFERENCES

1. Andrianov, K.A., Uspekhi Thimii., 26, No.8, 895 (1957)

2. Lachman, F., R.A.E. Translation No. 710 (Jan. 1958)

3. Brydson, J.A., Plastics, 22, 384 (1957).

4. Andrianov, K.A., Ganina, T., and Khrustaleva, E., Izvest. Akad. Nauk. S.S.S.R. Otdel. Khim. Nauk. 798, (1956)

5. Koenig, P.E., W.A.D.C. Tech. Rep. 58-44 Part I and II. (A.S.T.I.A. No. AD 151197, AD 215425) See also Rubber Chemistry and Technology 32, No.5, 1623 (1959)

6. Mack G.D. and Parker, E., U.S.P. 2, 626, 953 (1953) Chem. Abstr., 47, 11224 (1953).

7. Rothrock, H.S., U.S.P. 2, 258, 718 (1942) Chem. Abstr. 36, 595 (1942).

8. Langkammerer, C.M., U.S.P. 2, 253, 128 (1941) Chem. Abstr. 35, 8151 (1941).

9. Marks, B.M., U.S.P. 2, 687, 395 (1954) Chem. Abstr. 49, 2115 (1955).

10. Gloskey, C.R., Ind. and Eng. Chem., 49, No. 12, 47A (1957)

11. Korshak, V., Polyakova, A.M. and Tambovtseva, E.S., Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk., 742 (1959) Chem. Abstr. 54, 359 (b) (1960)

12. Andrews, T.M., Bower, F.A., La Liberte, B.R. and Montermoso, J.C., J. Amer. Chem. Soc. 80, 4102 (1958)

13. Noltes, J.G. and van der Kerk, G.J.M., Rec. trav. Chim. 81, 41 (1962), and 80, 623 (1961)

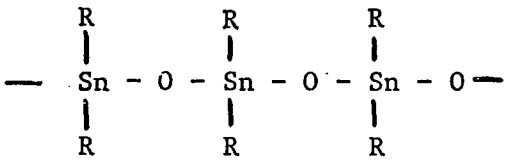
14. Department of the Army, USA (Quartermaster Corps). Consolidated Research and Development, Annual Project Report, Vol. 1. p317 (1957)

15. Montermoso, J.C. et al., Chem. and Eng. News. 36, No. 16, 50 (1958)

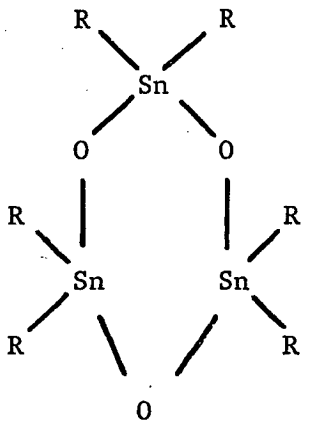
16. Montermoso, J.C., Andrews, T.M. and Marinelli, L.P., J. Polym. Sci. 32, No. 125, 523 (1958)

17. Shostakovskii, M.F., et al. J. Polym. Sci. 52, 223 (1961)

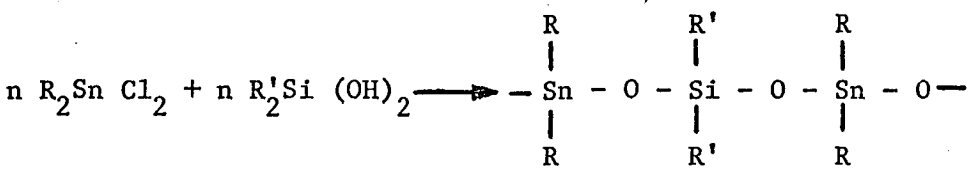
18. Luijten, J.G.A. and van der Kerk, G.J.M. "Investigations in the Field of Organotin Chemistry" (1955), p.54.



LINEAR POLYSTANNOXANES



CYCLIC POLYSTANNOXANES



LINEAR POLYSTANNOSILOXANES

Figure 1 - Some typical organotin polymers

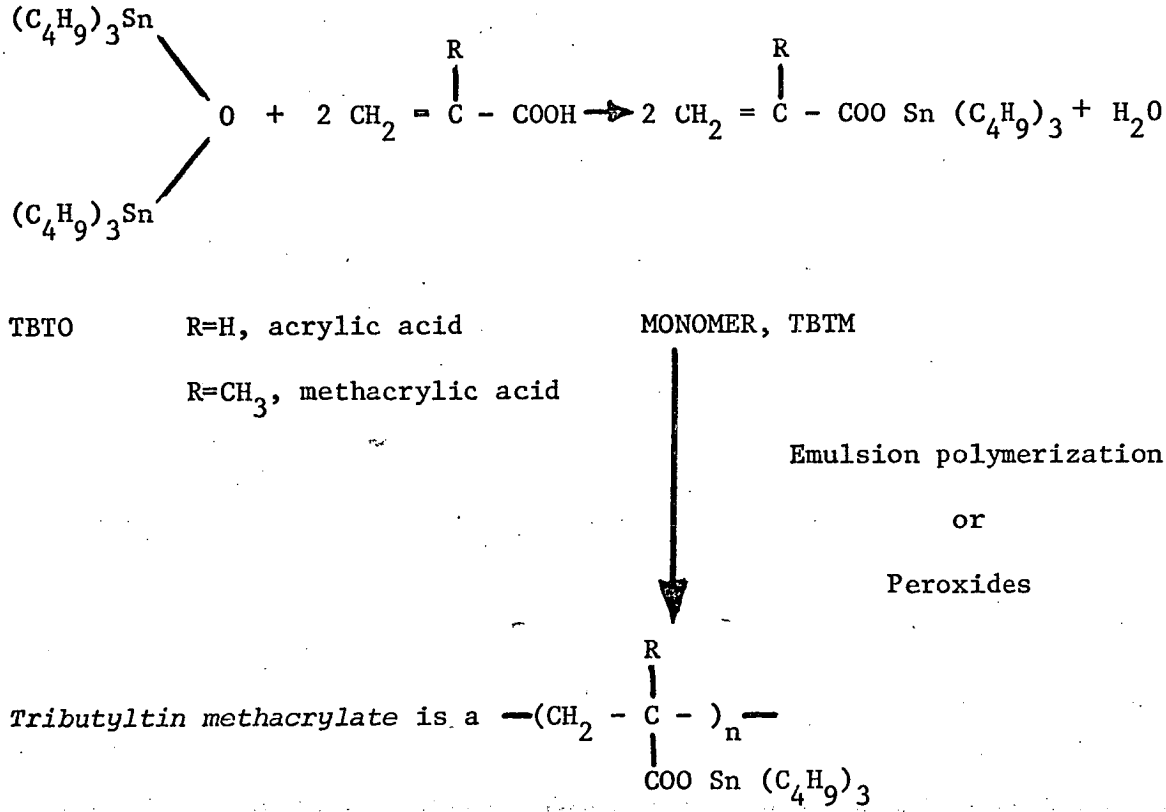


Figure 2 - Reaction sequence for the synthesis of organotin polymers

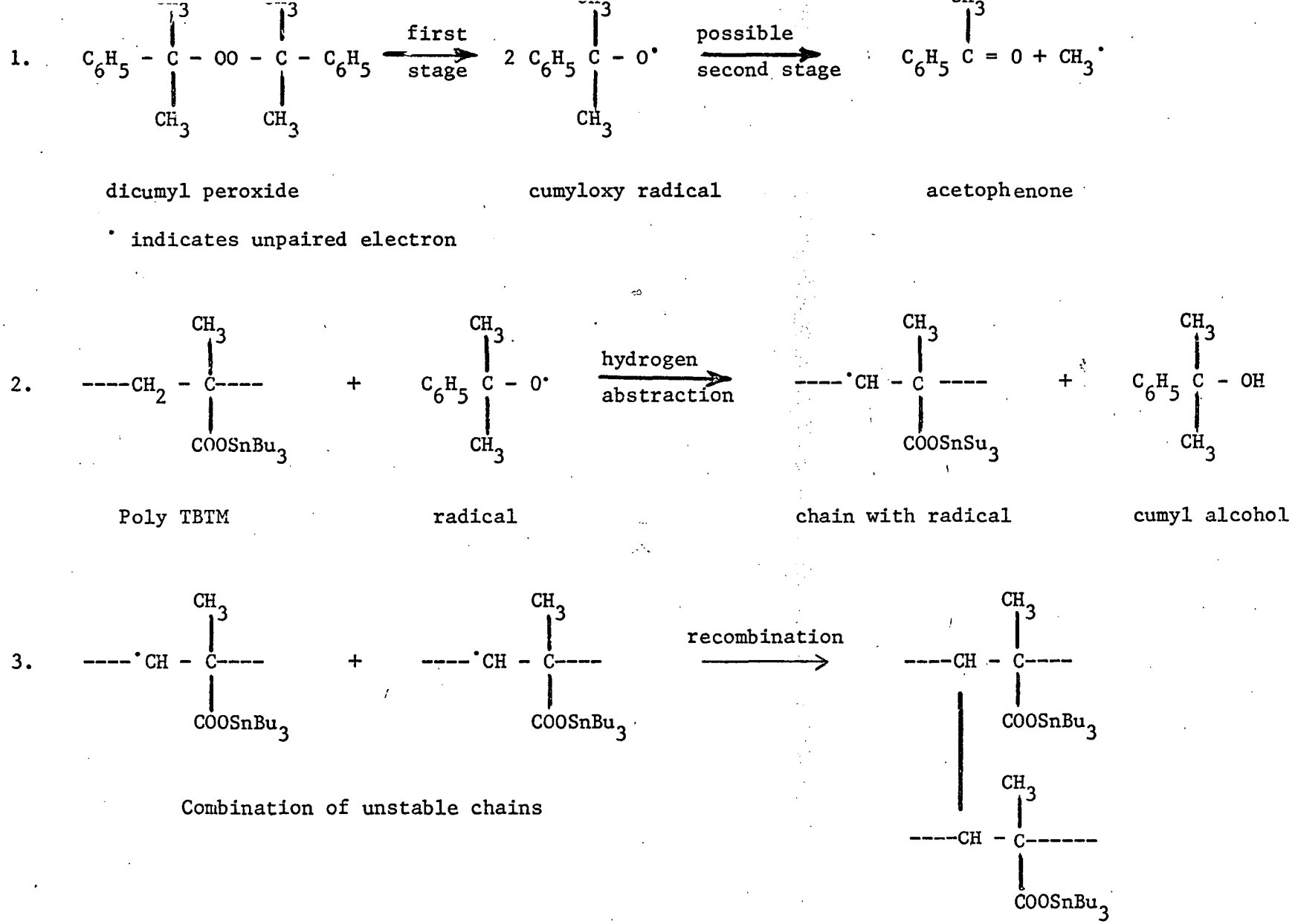


Figure 3 - Peroxide crosslinking of *poly(tributyltin methacrylate)*

TABLE 1

EMULSION POLYMERIZATION SYSTEMS FOR TRIBUTYLTIN METHACRYLATES

Tributyltin methacrylate	100	100
Water	180	200
*Tergitol NPX (non-ionic)	5	-
Sodium lauryl sulphate	-	3
Lauryl mercaptan	0.5	-
Ammonium persulphate	-	1.0
Potassium persulphate	0.5	-
Sodium bisulphate	-	0.1
Reaction time, h	9	6
Reaction temperature, ^{o}C	50	50
Coagulant	Alcohol	Acetone
Yield, %	80	72
Product	Tough rubber	Tough rubber

Copolymers with acrylonitrile (1:1) may also be made by the emulsion polymerization technique.

* Alkyl phenyl polyethylene glycol ether.

TABLE 2

CROSS-LINKING OF ORGANOTIN METHACRYLATES

Poly(tributyltin methacrylate)	100	100	98	100
Poly(dibutyltin dimethacrylate) (as a copolymer)	-	-	2	-
Dibutyltin oxide	-	10	10	-
Dibutyltin dihydride	-	2.5	2.5	-
Carbon black (HAF)	-	-	-	50
Dicumyl peroxide (40%)	-	-	-	4
Sulphur	-	3	3	-
Stannous chloride	-	-	1.5	-
Optimum cure (min/^{o}C)	-	45/250	30/250	30/125
Tensile strength, psi	125	400	300	320
Elongation at break, %	400	370	250	40
Volume change after 24 h immersion in isooctane at 25^{o}C, %	250	125	32	84

TABLE 3

EFFECT OF NUMBER OF ALKYL GROUPS ATTACHED TO TIN ON THE ANTIFUNGAL PROPERTIES OF ETHYLTIN COMPOUNDS. (FROM REF.18)

Tin Compound	*Botrytis allii*	*Penicillium italicum*	*Aspergillus niger*
$(C_2H_5)_4$ Sn	50 *	1000	100
$(C_2H_5)_3$Sn Cl	0.5	2	5
$(C_2H_5)_2$Sn Cl_2	100	100	500
C_2H_5Sn Cl_3	>1000	>1000	>1000
Sn Cl_4	>1000	>1000	>1000

* Concentration in ppm (mgm/l) causing complete inhibition of growth of fungi.

TABLE 4

INFLUENCE OF VARYING GROUP X ON THE ANTIFUNGAL PROPERTIES OF COMPOUNDS WITH THE GENERAL FORMULA $(C_2H_5)_3SnX$. (FROM REF.18)

Tin Compound	*Botrytis allii*	*Penicillium italicum*	*Aspergillus niger*
Triethyltin chloride	0.5 *	2	5
Triethyltin hydroxide	0.2	5	0.5
Bis(triethyltin) sulphide	0.2	1	1
Triethyltin acetate	1	2	5
Bis(triethyltin) maleate	0.5	5	0.5
Triethyltin phenoxide	0.5	1	2

* Concentration in ppm (mg/l) causing complete inhibition of growth of fungi.

TABLE 5

EFFECT OF POLY(TRIBUTYLTIN METHACRYLATE) ON SYNTHETIC RUBBER

INGREDIENT/PROPERTY	CONTROL	TEST COMPOUND
Polychloroprene (Neoprene WRT)	100	100
Zinc oxide	5	5
Magnesium oxide	4	4
Carbon black (MPC)	30	30
Stearic acid	2	2
Phenyl-β-naphthylamine	2	2
Dinonyl phthalate	8	-
2-Mercaptoimidazoline	1	1
Poly(tributyltin methacrylate) (33% in dinonyl phthalate)	-	12
Tear strength, lb/in thickness	220	215
Tensile strength, psi	2235	2035
Elongation at break, %	315	310
Hardness, ^{o}IRHD	63	60
Resistance to ozone attack, h to slight cracking (bent loop)	120	120

POLY(TRIBUTYLTIN METHACRYLATE) AS A FUNGICIDE FOR NATURAL AND SYNTHETIC RUBBER AND POLY(VINYL CHLORIDE)

MATERIAL	TYPE	Zone of fungal growth (+) or of fungal inhibition (-), mm			
		Aspergillus flavus DSL No. 283*	*Syncephalastrum Sp.* DSL No. 427	*Aspergillus niger* DSL No. 428	*Aspergillus tamarii* DSL No. 430
Polychloroprene Rubber (Neoprene)	Control	2	10	1	5
	Fungicide, 2.6%	-2	-1	-2	-2
Butadiene-acrylonitrile Rubber (Nitrile)	Control	0	-3	0	-3
	Fungicide, 2.3%	-5	-25	-3	-15
Styrene-butadiene Rubber (SBR)	Control	0	2	0	1
	Fungicide, 2.4%	-7	-12	-10	-25
Natural Rubber	Control	0	0	-10	0
	Fungicide, 2.4%	-8	-3	-5	-10
Plasticized Poly(vinyl chloride)	Control	+12	+5	+3	+4
	Fungicide, 0.5%	-3	0	0	-2

* Fungal strains from the DSL Culture Collection

APPENDIX 8b

ORGANOTIN COMPOUNDS AS FUNGICIDES FOR NATURAL AND SYNTHETIC RUBBERS*

As part of a programme to evaluate fungicides for plastics, several experiments were undertaken to determine the effectiveness of organotin compounds in various rubbers. At the same time the rubber compounds were tested in a standard atmosphere containing ozone in order that any antiozonant properties of the compounds might be determined.

Details of the rubber formulations used are as follows:-

1. Styrene - butadiene rubber (SBR)

Table 1 gives details of formulations and physical properties of vulcanizates made from SBR.

Table 1 Styrene - butadiene rubber

Ingredient	Mix JE/1	Mix JE/4	Mix JE/5
SBR (type 1006)	100	100	100
MPC carbon black	50	50	50
Zinc oxide	5	5	5
Sulphur	2	2	2
MBTS (benzothiazyl disulphide)	2	2	2
Stearic acid	2	2	2
Poly(tri-n-butyltin methacrylate)	-	4	-
Dibutyltin maleate	-	-	4
Optimum cure time, min at 150°C	25	25	25
Tear strength, lb/in thickness	-	285	293
Tensile strength, lb/sq in	2630	2335	2750
Elongation at break, %	510	410	470
Hardness, °IRHD	68	65	65
Resistance to ozone attack, h (To slight cracking)	18	23	23

*Laboratory work undertaken at DSL during 1961/62 and reported, in part, at ANZAAS, Sydney, 1962 (see Appendix 8a).

With mix JE/4, poly(tri-n-butyltin methacrylate) rubber was compounded into the rubber mix without any difficulty. With mix JE/5, the introduction of dibutyltin maleate caused the rubber stock to become very soft and tacky. The incorporation of the last ingredient sulphur, by blending, was carried out with considerable difficulty.

2. Natural rubber

Table 2 gives details of formulations and physical properties of vulcanizates made from natural rubber.

Table 2 Natural rubber

Ingredient	Mix A253	Mix A253/1	Mix A253/2
Smoked sheet, No.1	100	100	100
Calcium carbonate, coated (Winnofil)	50	50	50
Zinc oxide	5	5	5
Stearic acid	0.5	0.5	0.5
TMT (tetramethyl thiuram disulphide)	0.3	0.3	0.3
MBT (2-mercaptobenzothiazole)	0.7	0.7	0.7
Sulphur	2.5	2.5	2.5
Agerite White (di-β-naphthyl-p-phenylenediamine)	2	2	2
Poly(tri-n-butyltin methacrylate)	-	4	-
Dibutyltin maleate	-	-	4
Optimum cure time, min at 150°C	8	8	7
Tear strength, lb/in thickness	235	286	330
Tensile strength, lb/sq in	2055	2760	3260
Elongation at break, %	550	620	570
Hardness, °IRHD	49	49	56
Resistance to ozone attack, h (To slight cracking)	24	24	24

On the rubber mill the three natural rubber compounds behaved similarly to the styrene-butadiene compounds.

3. Polychloroprene rubbers (CR)

Table 3 gives details of formulations and physical properties of vulcanizates made from CR.

Table 3 Polychloroprene rubber

Ingredient	Mix A258	Mix A258/1	Mix A258/2	Mix A258/3
Polychloroprene (Neoprene WRT)	100	100	100	100
Zinc oxide	5	5	5	5
Magnesium oxide	4	4	4	4
MPC carbon black	30	30	30	30
Stearic acid	2	2	2	2
Nonox D (phenyl-β-naphthylamine)	2	2	2	2
Dinonyl phthalate	8	-	8	8
NA22 (2-mercapto-imidazoline)	1	1	1	1
Poly(tri-n-butyltin methacrylate) (33% soln. in dinonyl phthalate)	-	12	-	-
Dibutyltin maleate	-	-	4	-
Bis(tri-n-butyltin) maleate	-	-	-	4
Optimum cure time, min at 155°C	25	35	30	30
Tear strength, lb/in thickness	220	215	220	206
Tensile strength, lb/sq in	2235	2035	2090	2235
Elongation at break, %	315	310	330	380
Hardness, °IRHD	63	60	58	56
Resistance to ozone attack, h (To slight cracking)	120	120	120	120

With Mix A258/1, the fungicide was incorporated using a 33% solution of poly(tri-n-butyltin methacrylate) in dinonyl phthalate. By this means better dispersion of the fungicide was obtained than if the fungicide was added in the form of a pure polymer. Bis(tri-n-butyltin) maleate was added without difficulty but, as in the case of the styrene-butadiene rubbers and of the natural rubbers, the addition of dibutyltin maleate resulted in the mix becoming soft and very tacky.

4. Butadiene - acrylonitrile rubbers (NBR)

Table 4 gives details of formulations and physical properties of vulcanizates made from NBR.

Table 4 Butadiene - acrylonitrile rubber

Ingredient	Mix A244	Mix A244/2	Mix A244/3	Mix A244/4
Butadiene-acrylonitrile rubber (Breon 1041)	100	100	100	100
HAF carbon black	45	45	45	45
TMT (tetramethyl thiuram disulphide)	3	3	3	3
MBTS (benzothiazyl disulphide)	3	3	3	3
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Nonox D (phenyl-β-naphthylamine)	2	2	2	2
Dibutyl phthalate	10	10	10	10
Poly(tri-n-butyltin methacrylate)	-	4	-	-
Dibutyltin maleate	-	-	4	-
Bis(tri-n-butyltin) maleate	-	-	-	4
Optimum cure time, min at 155°C	30	30	30	75
Tear strength, lb/in thickness	305	305	230	245
Tensile strength, lb/sq in	3010	2355	1435	1730
Elongation at break, %	830	800	1090	1000
Hardness, °IRHD	58	58	55	56
Resistance to ozone attack, h (To slight cracking)	22	23	20	18

In compounding the butadiene-acrylonitrile rubbers on the mill, no trouble was experienced on adding the fungicides to the mix. Bis(tri-n-butyltin) maleate and dibutyltin maleate could be added without the mix becoming soft and tacky. However the addition of maleate derivatives to this type of synthetic rubber caused considerable retardation of the cure and consequent reduction in the tensile strength of the vulcanizate.

5. Effect on compounding and ozone resistance

In all rubbers, poly(tri-n-butyltin methacrylate) could be added at a level of 4 parts of fungicide per 100 parts of rubber without adversely affecting the physical properties of the rubber. No difficulties were encountered during processing, but generally better dispersion of the fungicide could be obtained when the material was added in the form of a 33% solution in dinonyl phthalate rather than as 100% fungicide.

In general, organotin compounds had more effect on butadiene - acrylonitrile rubbers than on the other types tested. Dibutyltin maleate and bis(tri-n-butyltin) maleate, markedly affected the rate of cure and resulted in poor quality vulcanizates. With natural rubber, polychloroprene rubber and styrene - butadiene type rubber the addition of organotin maleates caused the mix to become soft and sticky and rather difficult to handle on the mill. However these maleate compounds had no marked effect on the physical properties of the finished rubbers.

The resistance of the compounded rubbers to ozone attack was evaluated by exposing tensile strength test pieces under dynamic conditions in an atmosphere containing 1 ppm of ozone at a temperature of 50°C. The test pieces were stretched to 20% elongation at a rate of 25 cycles per min during exposure.

With all rubbers there were no marked changes in the time taken to develop slight cracking between the control compounds, and those compounds containing organotin compounds. None of the compounds tested show any significant antiozonant activity.

6. Assessment of fungicidal activity of organotin compounds

As a result of previous experiments with various fungi obtained from the DSL Culture Collection, four fungi were selected as test organisms. Details are given in Table 5.

Test specimens of rubber sheet were cut using a 50 mm x 25 mm standard cutter and after cleaning, the specimens were placed on the surface of a sterile layer of Czapek's medium in a petrie dish. After spraying with a suspension of fungal spores of the test organism, the agar plates were incubated for 14 days at 30°C. The activity of the fungicide was then assessed by measuring the zone of growth or inhibition produced by the fungi. A figure of 0 indicates that the fungus was growing up to the edge of the test specimen but not growing on the specimen surface. A positive figure indicates the fungus was growing on the surface of the test specimen while a negative figure indicates that a fungus-free zone surrounded the test specimen.

As shown in Table 5, natural rubber and butadiene-acrylonitrile rubber formulations containing no fungicide show good resistance to fungal attack. This is not unexpected, since they both contain tetramethyl thiuram disulphide as part of the accelerator system and this compound is reported to have fungicidal properties (1). Since the butadiene-acrylonitrile control contains a higher percentage of tetramethyl thiuram disulphide than the natural rubber control the fungicidal resistance of the acrylonitrile rubber is generally better than that of the natural rubber. Styrene-butadiene rubbers are only slightly attacked by fungi, but polychloroprene rubbers have very poor resistance to fungal attack. In general the fungicidal resistance of the control rubbers was in the order: butadiene-acrylonitrile, natural rubber, styrene-butadiene, polychloroprene.

The introduction of poly(tri-n-butyltin methacrylate) or bis(tri-n-butyltin) maleate increased the fungal resistance of the control formulation. No fungal growth occurred on any of the rubbers that contained either of the trialkyltin compounds as fungicides. On the other hand, dibutyltin maleate was generally ineffective as a fungicide. This is not unexpected as dialkyltin compounds normally exhibit very low fungal activity as compared to the corresponding trialkyltin compounds.

In these experiments, fungicides were added at a level of 4 parts per 100 parts of rubber. Experiments with poly(vinyl chloride) indicate that adequate protection can be obtained at lower concentrations, and a level of 0.5 to 1.0 part of fungicide per 100 parts of rubber should be adequate for most purposes.

7. Conclusions

(a) Trialkyltin compounds can be added to natural and synthetic rubbers to give effective protection against fungal attack.

(b) The incorporation of poly(tri-n-butyltin methacrylate) into a rubber formulation can be made either using 100% active compound or as a 33% solution of the compound in dinonyl phthalate.

(c) The use of poly(tri-n-butyltin methacrylate) or bis(tri-n-butyltin) maleate at 4 pphr in natural rubber, styrene-butadiene rubber and polychloroprene rubber does not markedly affect the properties of these rubbers. In the case of butadiene - acrylonitrile type rubbers the use of bis(tri-n-butyltin) maleate has a profound effect on the rate of cure of the compound.

(d) Dibutyltin maleate in general affects the processing characteristics of some rubbers. It has a slight accelerating effect in natural rubber and shows little, if any, fungidical action.

(e) The use of organotin compounds in rubber formulations does not appear to affect the resistance of the compounds to attack by ozone.

8. References

1. Yashish, V.B. Selection of Fungicides for Materials Used in the Cable Industry. Kabel'naya Teckh. 1957, No.1-2, 42-6. (Chem.Abs.54,25487(b),(1960))

TABLE 5 - FUNGICIDAL TESTS ON RUBBERS - EVALUATION AFTER 14 DAYS INCUBATION

Elastomer	Fungicide	Mix No.	Zone of fungal growth (+) or zone of fungal inhibition (-), mm			
			Aspergillus flavus Culture No.283	*Syncephalastrum sp.* Culture No.427	*Aspergillus niger* Culture No.428	*Aspergillus tamarii* Culture No.430
Styrene - butadiene	Nil	JE/1	0	+2	0	+1
	Poly TBTM(a)	JE/4	-7	-12	-10	-25
	DBTM(b)	JE/5	0	+1	0	0
Natural	Nil	A253	0	0	-10	0
	Poly TBTM	A253/1	-8	-3	-5	-10
	DBTM	A253/2	-2	-1	-1	-1
Polychloroprene	Nil	A258	+2	+10	+1	+5
	Poly TBTM	A258/1	-2	-1	-2	-2
	DBTM	A258/2	0	+6	0	0
	Bis TBTM(c)	A258/3	-2	-5	-2	-3
Butadiene - acrylonitrile	Nil	A244	0	-3	0	-3
	Poly TBTM	A244/2	-5	-25	-3	-15
	DBTM	A244/3	-4	-5	-2	-4
	Bis TBTM	A244/4	-12	-25	-4	-13

(a) Poly TBTM : Poly(tri-n-butyltin methacrylate)

(b) DBTM : Dibutyltin maleate

(c) Bis TBTM : Bis(tri-n-butyltin) maleate

APPENDIX 8c

COPOLYMERS OF TRIBUTYLTIN METHACRYLATE AND CHLOROETHYL VINYL ETHER

Preparation of copolymers of tributyltin methacrylate and chloroethyl vinyl ether was investigated using both emulsion polymerization and peroxide polymerization techniques.

1. Emulsion Polymerization (Polymer 6, Poly TBTM (EP))

A mixture of tributyltin methacrylate and chloroethyl vinyl ether (95:5, by weight) was emulsion polymerized using the following formulation:-

Material	Weight (g)
Tributyltin methacrylate (a)	474
Chloroethyl vinyl ether (b)	23.7
Distilled water	1000
Aerosol OT (c)	9.96
Tergitol 4 (d)	39.84
Ammonium persulphate ($(NH_4)_2S_2O_8$)	0.025

(a) Synthesized at DSL
(b) Material ex Union Carbide Aust. Ltd.
(c) Sodium dioctyl sulpho-succinate (100%)
(d) Sodium tetradecyl sulphonate (25%)

The mixture was heated with continuous stirring at 90°C for 5h. The emulsion was then steam distilled for 30 min and the coagulated polymer removed and dried under vacuum at 70°C. Yield, 366g (74%).

The polymer contained 0.1% by weight, of chlorine, equivalent to 0.3% chloroethyl vinyl ether. These figures indicate that very little copolymerization had occurred. Attempts to crosslink the polymer using the formulations given in Table 1 were unsuccessful.

Although Polymer 6 was a transparent elastic solid, all the compounded samples showed excessive blowing and poor physical properties.

2. Peroxide Polymerization (Poly TBTM(PP))

A 95:5 mixture of tributyltin methacrylate (TBTM) and chloroethyl vinyl ether (CEVE) monomers was treated with 1%, by weight of various peroxides (equivalent to 100% active) and then heated under nitrogen at 70°C for 24h followed by a further heating at 105°C for 72h. The samples were analysed for chlorine by a Parr bomb fusion followed by precipitation of the chloride as silver chloride. Results are given in Table 2.

TABLE 1. Compounding Studies on Organotin Copolymers

Formulation Number	400 - 6.0	400 - 6.1	400 - 6.2	400 - 6.3	400 - 6.4
Polymer 6	100	100	100	100	100
Carbon black, Acarb SRF	-	30	30	30	30
TETA (a)	-	1.25	-	-	-
HMDA carbamate (b)	-	2.5	-	-	-
Stearic acid	-	-	1.0	-	3.0
Sulphur	-	-	0.5	1.0	-
Trimene base (c)	-	-	3.0	-	-
Hexachloroethane	-	-	-	5.0	-
Iron oxide (stearic acid coated)	-	-	-	5.0	-
GMF (d)	-	-	-	-	2.0
Lead oxide, red	-	-	-	-	10.0
Poly(butyl methacrylate)	-	10.0	10.0	10.0	10.0
Total	100	143.75	144.5	151.0	155.0
Press cure (min/°C)	30/160	30/160	30/160	30/160	30/160

(a) Triethylene tetra-amine (Shell Chemicals)
(b) Hexamethylene diamine carbamate (Diak No.1 - Du Pont)
(c) Ethyl chloride, formaldehyde, ammonia reaction product
(d) p-Quinonedioxime (Uniroyal Chemicals)

Small cylindrical pellets of the copolymers were heated at 105°C for 6h and the effects of heating noted. Copolymers made using Dicup R, PX60, Varox, DTBP and K1960 retained their shape while those made using MEKP and TBHP were only slightly affected. Copolymers made using benzoyl peroxide, 2,4-DCBP, S890 and Genetron AZDN were thermoplastic at 105°C.

In order to determine the effect of concentration of peroxide on the polymerization of the comonomers a 95:5 mixture of tributyltin methacrylate and chloroethyl vinyl ether was polymerized with varying concentrations of benzoyl peroxide. The samples were heated under nitrogen at 70°C for 24h, followed by heating at 105°C for 72h. In all cases a yield of 97% of the copolymer was obtained, and the chloroethyl vinyl ether content in the polymer ranged from 2.4% to 3.2% by weight, depending on the concentration of peroxide used. Results are given in Table 3.

TABLE 2. Peroxide Polymerization of Comonomers

Peroxide/Activity (%)	Yield of copolymer, %	Chlorine found, %	CEVE equivalent, %
Benzoyl peroxide (100)	96	1.08	3.24
Methyl ethyl ketone peroxide, MEKP (35)	95	0.80	2.40
Dicup 40 C (dicumyl peroxide, 40)(a)	98	1.9	5.70
Dicup R (dicumyl peroxide, 100)(a)	97	0.70	2.10
2,4-Dichlorobenzoyl peroxide, DCBP (50)	97	1.19	3.57
Montecatini PX60 peroxide (100)	97	0.60	1.80
Ditertiarybutyl peroxide, DTBP (100)	94	0.63	1.89
Hercules, S 890 peroxide (100)	97	0.44	1.32
Tertiary butyl hydroperoxide, TBHP (75)	93	0.67	2.01
Azobis-isobutyronitrile, AZDN (100)	96	0.69	2.07
Union Carbide, K1960 peroxide (40)	96	0.50	1.50
Varox (40), (b)	97	0.81	2.43

(a) Hercules Powder Company
(b) 2,5-Bis(tert-butylperoxy)-2,5-dimethyl hexane (Vanderbilt)

TABLE 3. Effect of Peroxide Content on Polymerization

Concentration of benzoyl peroxide in a 95:5 TBTM/CEVE monomer blend, %	Yield of polymer, %	Chlorine found, %	CEVE equivalent in polymer, %
0.04	97	0.95	2.9
0.20	97	0.80	2.4
1.0	97	1.05	3.2
5.0	97	1.00	3.0

To investigate the effect of concentration of chloroethyl vinyl ether on the preparation of tributyltin methacrylate - chloroethyl vinyl ether copolymers, several copolymers were prepared using benzoyl peroxide, 1% by weight, as the polymerizing agent. The mixed monomers were heated at 70°C for 24h followed by heating at 105°C for 72h.

The results (Table 4) indicate that as the percentage of CEVE in the monomers is increased, a greater percentage of CEVE is retained in the copolymer. Copolymers containing higher amounts of CEVE are soft, very elastic materials while those with lower amounts of CEVE are tough and rubberlike. The copolymer based on TBTM/CEVE monomers in the ratio 90:10 and polymerized using 1% benzoyl peroxide could warrant further investigation.

TABLE 4. Effect of Chloroethyl Vinyl Ether Content on Copolymerization

CEVE per 100 parts of monomers, %	Yield of polymer, %	Chlorine found, %	CEVE equivalent in polymer, %
5	97	1.05	3.2
10	95	2.5	7.5
15	94	3.7	11.1
20	92	4.2	12.6

APPENDIX 9 SYNTHESIS OF NEW ORGANOTIN COMPOUNDS

9a The Preparation of Organotin Compounds.
P. DUNN and T. NORRIS
Report 269. Defence Standards Laboratories
Department of Supply, Melbourne, Victoria. 9.2 - 9.25

Tables 1, 3 and 6 have been retyped to suit the format of A4 size paper.

APPENDIX 9

REPORT 269

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REPORT 269

THE PREPARATION OF ORGANOTIN COMPOUNDS

P. DUNN and T. NORRIS

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AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
DEFENCE STANDARDS LABORATORIES

REPORT 269

THE PREPARATION OF ORGANOTIN COMPOUNDS

P. DUNN and T. NORRIS

SUMMARY

The preparation of about sixty new organotin compounds is described. The compounds are mono-, di- and trialkyl and aryl organotins containing carboxyl, fluoride, chloride, oxide, hydroxide, hydride and other miscellaneous groups.

Analytical procedures for characterizing certain organotin compounds are given.

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THE PREPARATION OF ORGANOTIN COMPOUNDS

1. INTRODUCTION

The reviews by Ingham, Rosenberg and Gilman (1) and Neumann (2) and the reports by Luijten and van der Kerk (3) and by Noltes and van der Kerk (4) show that well over 700 organotin compounds have been synthesised, and many of them have been described in detail.

However as part of studies on the infrared and fungicidal properties of organotin compounds some new materials were required. The compounds prepared were mono, di and trialkyl and aryl organotins, containing carboxyl, fluoride, chloride, oxide, hydroxide, hydride and other miscellaneous groups. This report while taking previous work into account discusses various reactions of organotin compounds and describes the preparation of these new compounds.

2. DISCUSSION

2.1 Trialkyltin Carboxylates

Although over 30 triethyltin carboxylates have been reported by Ingham and coworkers (1), very few tributyltin carboxylates have been reported. Luijten and van der Kerk (3) have described the fungicidal properties of tributyltin acetate and cyanoacetate, while tributyltin laurate is commercially available as a fungicide. Alleston and Davies (5) have reported the preparation of tributyltin octanoate (caprylate) and Montermoso, Andrews and Marinelli (6) have prepared and polymerized tributyltin methacrylate and acrylate.

Tributyltin carboxylates are readily prepared by the action of organic acids on bis-(tributyltin) oxide.

$$(C_4H_9)_3\ Sn\text{-}O\text{-}Sn\ (C_4H_9)_3 + 2R.COOH \rightarrow 2(C_4H_9)_3\ Sn.OOC.R + H_2O$$

Saturated, unsaturated and substituted alkyl and aryl organic acids react without difficulty, and the carboxylates may be purified by crystallization or distillation.

In Table 1 are listed some of the properties of a series of tributyltin saturated carboxylates. Although tributyltin formate is a mobile liquid the acetate, propionate, butyrate, isobutyrate, valerate, isovalerate, caproate, isocaproate, heptylate, caprylate

and pelargonate are white crystalline low melting solids while the caprate, undecanoate, laurate, tridecylate, myristate, pentadecylate, palmitate, margarate and stearate are viscous liquids or semi solids.

Details of six new tributyltin (and one trioctyltin) unsaturated carboxylates and of thirteen new tributyltin substituted carboxylates are given in Tables 2 and 3 respectively. Most of these compounds are low melting solids, that can be purified by crystallization from petroleum ether or by sublimation.

2.2 Bis(tributyltin) carboxylates

Aliphatic and aromatic dicarboxylic acids react with bis(tributyltin) oxide to form carboxylates that are insoluble in many common organic solvents.

$$(Bu_3Sn)_2O + R(COOH)_2 \rightarrow Bu_3Sn.OOC.R.COOSnBu_3 + H_2O$$

Twelve bis(tributyltin) carboxylates have been prepared and details of these are given in Table 4. Bis(tributyltin) maleate is a viscous liquid when freshly prepared but on standing for several days changes to a low melting point solid. This solid could be the true form of the maleate, could be caused by polymerization, or could be bis(tributyltin) fumarate formed by isomerization. This last possibility is not consistent with the observations that the melting points and infrared spectra of the solid maleate and the fumarate are different.

Bis(tributyltin) terephthalate was obtained as a white crystalline solid, and bis(tributyltin) phthalate was a viscous liquid that decomposed on distillation.

2.3 Miscellaneous Organotin Carboxylates

Although bis(triethyltin) carbonate has been reported (1, Table 20) as a solid, m.p. 120°C., bis(tributyltin) carbonate, prepared by bubbling carbon dioxide through an alcoholic solution of the oxide, is a sticky solid that decomposes with the liberation of carbon dioxide when heated.

$$(C_4H_9)_3\,Sn\text{-}O\text{-}Sn\,(C_4H_9)_3 + CO_2 \rightleftharpoons (C_4H_9)_3\,Sn\text{-}OCO\text{-}Sn\,(C_4H_9)_3$$
$$\qquad\qquad\qquad

Aromatic dicarboxylic acid half esters also react with bis(tributyltin) oxide to form carboxylates. Monomethyl and monobutyl(tributyltin) phthalate have been prepared by this method.

$$(Bu_3Sn)_2O + 2CH_3OOCC_6H_4\ COOH \rightarrow 2CH_3OOCC_6H_4\ COOSn\ Bu_3 + H_2O$$

Ingham and coworkers (1, Table 18) describe many dialkyltin carboxylates, which are prepared from dialkyltin oxides by reaction with the appropriate acids.

$$R_2Sn = O + 2R^1COOH \rightarrow R_2Sn\ (OOCR^1)_2 + H_2O$$

Many dialkyltin unsaturated dicarboxylates such as dioctyltin diacrylate and dimethacrylate polymerize on heating to form high molecular weight compounds (6).

Details of twelve miscellaneous organotin carboxylates are given in Table 5.

2.4 Organotin Oxides and Hydroxides

Although many organotin oxides and hydroxides have been reported, (1, Tables 14, 15 and 19) the structure of some of these compounds is in doubt. In general the alkyl and aryl stannonic acids ($RSnOOH$) and the dialkyltin oxides are white infusible, insoluble powders that exist mainly in the form of long chain, and cyclic, polymeric compounds. The diaryl, triaryl, and trialkyltin oxides and hydroxides usually exist as monomeric liquids or low melting solids.

Butyltin trichloride on reaction with sodium hydroxide solutions, forms butyl stannonic acid, $C_4H_9Sn(=O)\cdot OH$, rather than the bis(butyltin) oxide, $C_4H_9Sn(=O)\cdot O\cdot(=O)\ SnC_4H_9$. The reaction product, butyl stannonic acid, was confirmed by analysis and infrared examination. Polymeric phenyl stannonic acid is formed by a similar reaction.

Although triphenyltin hydroxide has been known for some time, only recently have attempts been made to determine its structure. The hydroxide is prepared by reaction of sodium hydroxide with triphenyltin chloride. However, triphenyltin hydroxide can be readily dehydrated to form bis(triphenyltin) oxide and in many cases mixtures of the oxide and hydroxide have been reported. The reactions are:

$$(C_6H_5)_3\ SnCl + NaOH \rightarrow (C_6H_5)_3\ SnOH + NaCl$$

$$2(C_6H_5)_3\ SnOH \underset{-H_2O}{\rightleftharpoons} (C_6H_5)_3\ Sn\text{-}O\text{-}Sn\ (C_6H_5)_3 + H_2O$$

Recent preparative and infrared studies by West, Baney and Powell (7), Poller (8) and Friebe and Kelker (9) have helped to elucidate the composition of triphenyltin hydroxide and oxide. Details of compounds prepared are given in Table 6.

2.5 Organotin Hydrides

Organotin hydrides can be prepared by the reaction of lithium aluminium hydride on alkyl and aryltin halides. Noltes and van der Kerk (4, Table 11) have reported many organotin hydrides, and dioctyltin dihydride has now been prepared by the reduction of dioctyltin dichloride, viz.,

$$2\ (C_8H_{17})_2\ SnCl_2 + LiAlH_4 \rightarrow 2\ (C_8H_{17})_2\ SnH_2 + LiCl + AlCl_3$$

Noltes and van der Kerk (4) prepared tributyltin hydride by the reduction of tributyltin chloride, but this compound may also be obtained in good yields by the reduction of bis(tributyltin) oxide with lithium aluminium hydride.

2.6 Organotin Halides

Ingham, Rosenberg and Gilman (1, Tables 7, 8, 9 and 10) have reported the preparation of alkyl and aryltin fluorides, and, in most cases, the compounds have been prepared by the reaction of potassium fluoride or hydrofluoric acid with the appropriate chloride, bromide or iodide of the organotin compound. We have now found that the organotin fluorides can be readily prepared by the reaction of ammonium fluoride with an organotin chloride or oxide. Tributyltin fluoride is prepared as follows:

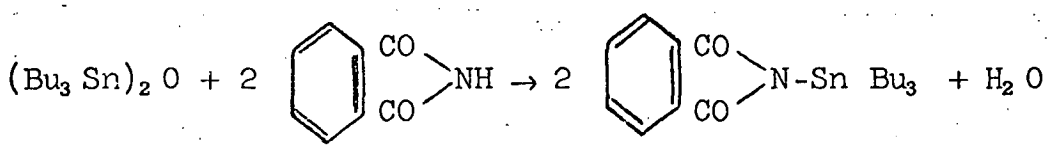
$$(C_4H_9)_3\ Sn\text{-}O\text{-}Sn\ (C_4H_9)_3 + NH_4F \rightarrow (C_4H_9)_3\ SnF \leftarrow NH_4F + (C_4H_9)_3\ SnCl$$

Similarly dibutyltin difluoride (5) can be prepared in good yields by the reaction of ammonium fluoride with dibutyltin dichloride, and triphenyltin fluoride can be prepared by the reaction of the same fluorinating agent with triphenyltin chloride, oxide or hydroxide.

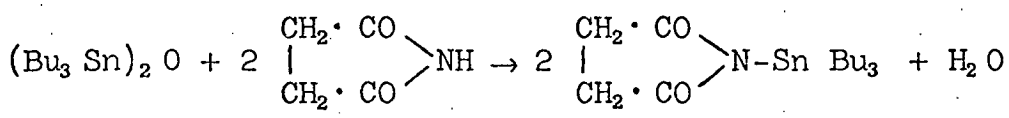
Although many mono-alkyl and mono-arylorganotin trichlorides, bromides and iodides have been reported (1, Table 12) our attempts to prepare a pure trifluoride compound were unsuccessful. Ammonium fluoride reacts vigorously with butyl or phenyltin trichlorides, but the crude wax-like products could not be purified.

2.7 Organotin Compounds Containing Nitrogen

Ingham, Rosenberg and Gilman (1, Table 20), van der Kerk and coworkers (10, 11) and Abel, Brady and Lerwill (12) have reported new nitrogen containing organotin compounds. We have made new compounds of this type by preparing tributyltin phthalimide, tributyltin succinimide and tributyltin isothiocyanate. These compounds are prepared as follows:



$$(Bu_3Sn)_2O + 2\ \text{phthalimide} \rightarrow 2\ \text{N-Sn Bu}_3\text{ phthalimide} + H_2O$$



$$(Bu_3Sn)_2O + 2\ \text{succinimide} \rightarrow 2\ \text{N-Sn Bu}_3\text{ succinimide} + H_2O$$

Tributyltin isothiocyanate may be prepared by the reaction of potassium, silver or ammonium thiocyanate on tributyltin chloride, or on a mixture of bis(tributyltin) oxide and dilute hydrochloric acid.

$$(C_4H_9)_3\ SnCl + M\ SCN \rightarrow (C_4H_9)_3\ Sn\ NCS + M\ Cl$$

where M: = Ag, K, or NH_4.

Tributyltin isothiocyanate can also be formed from tributyltin cyanide (3) by reaction of sulphur dissolved in carbon disulphide.

Bis(tributyltin) oxide will also react with thiourea to give tributyltin isothiocyanate and bis(tributyltin) sulphide, ammonia and water also being formed.

The main product from this reaction is bis(tributyltin) sulphide, formed by an interchange between oxygen and sulphur.

$$(Bu_3Sn)_2O + NH_2 \cdot C(=S) \cdot NH_2 \rightarrow Bu_3\ SnNCS + H_2O + NH_3 + Bu_3\ Sn\text{-}S\text{-}Sn\ Bu_3$$

Substituted thioureas such as diphenyl, diethyl and dibutyl thiourea also react with bis(tributyltin) oxide to give goods yields of bis(tributyltin) sulphide.

Although bis(tributyltin) oxide will not react with pyridine, or pyrrole, the oxide will react with acetamide and benzamide with the liberation of water. The reaction product from bis(tributyltin)

xide and acetamide can be distilled under vacuum, but is hydro-ytically unstable, and even in the presence of slight traces of ater, acetamide is reformed.

$$(Bu_3Sn)_2O + 2\ CH_3\cdot CONH_2 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} 2\ CH_3\cdot CO\cdot NHSn\ Bu_3 \quad \text{(unstable)}$$

Many nitrogen containing organotin addition compounds are known 1, Table 21), and dibutyltin dichloride dipyridinate has been re-orted by Pfeiffer and coworkers (13). Tributyltin chloride onopyridinate and butyltin trichloride dipyridinate have now been repared by reaction of the organotin chloride and pyridine. The eactions are:

$$C_4H_9\ Sn\ Cl_3 + 3\ C_5H_5N \rightarrow C_4H_9\ SnCl_3.2\ C_5H_5N + C_5H_5N$$

$$(C_4H_9)_3\ Sn\ Cl + C_5H_5N \rightarrow (C_4H_9)_3\ Cl.C_5H_5N$$

Several trialkyltin nitrates have been reported (1, Table 20; 4) but attempts to prepare tributyltin nitrate by the reaction of itric acid on bis(tributyltin) oxide resulted in oxidation of the rganotin compound to stannic oxide. Reaction of silver nitrate ith tributyltin chloride according to the sequence,

$$(C_4H_9)_3\ Sn\ Cl + AgNO_3 \rightarrow (C_4H_9)_3\ Sn\ ONO_2 + AgCl$$

ave good yields of tributyltin nitrate.

Details of the nitrogen - containing organotin compounds that ere prepared are given in Table 6.

3. EXPERIMENTAL

.1 Analytical Procedures

The analysis of organotin compounds has been discussed by ngham, Rosenberg and Gilman (1) and details of the methods we used o determine tin, chlorine, fluorine, nitrogen and sulphur are as ollows:

.1.1 Tin Content

About 150 mg of the organotin compound was weighed into a tall) ml beaker, and carefully treated with 3.0 ml of a freshly pre-ared oxidizing solution consisting of equal parts of fuming nitric id and fuming sulphuric acid. The beaker was gently heated to

complete the oxidation reaction, care being taken to avoid overheating of any volatile compounds. When the evolution of nitrous vapours ceased, excess sulphuric acid was fumed off. After removal of all the acid, the beaker was heated in a blast-burner flame. After cooling in a desiccator, the stannic oxide residue was weighed and the tin content calculated.

With the organotin carboxylates erratic results were obtained using the method described above, and for these compounds a modified method was used.

About 500 mg of the organotin carboxylate was weighed into a 60 ml silica crucible which was cooled in a tray of water to prevent overheating. A solution of bromine in carbon tetrachloride (4% by weight) was added dropwise until an excess of bromine persisted. The brominated compound was then carefully treated with oxidizing solution as described above and the tin present ignited and weighed as stannic oxide. Overheating during the bromination and oxidation had to be avoided in order to ensure reproducible results.

3.1.2 Chlorine Content

An accurately weighed sample of the organotin chloride (about 300 mg) was dissolved in ether (20 ml) and shaken three times with 20% aqueous sodium hydroxide (20 ml each), and then washed twice with water. The combined extracts and washings were neutralized with concentrated nitric acid and an excess then added (5 ml). An aqueous solution of silver nitrate (20%) was then slowly added until precipitation of the silver chloride was complete and a small excess of silver nitrate then added. After boiling the solution for several minutes the precipitate was filtered through a Gooch crucible, washed with 1% nitric acid, and then dried at 130°C.

The above method can be used to determine only halogen directly attached to tin in an organotin compound. Where the chlorine is attached to carbon in an organotin compound, however, for example tributyltin monochloroacetate, the sample must first be decomposed by a Parr bomb fusion (see Section 3.1.5), and chloride then determined gravimetrically as silver chloride.

3.1.3 Fluorine Content

A weighed sample of organotin fluoride (approximately 600 mg) was refluxed for 1.5 hr. with 20% alcoholic potash (50 ml) cooled and washed three times in a separating funnel with chloroform (75 ml each). The aqueous extracts and washings from the chloroform were combined, evaporated to 200 ml and made acid to methyl red indicator with dilute nitric acid. Sodium hydroxide (1N) was then added until the solution was just alkaline, and a few drops of 30% acetic acid added until the solution was just acid to methyl red. The boiling solution was then treated with an equal volume of boiling saturated lead chloride to precipitate the fluoride as lead

chlorofluoride. The solution was allowed to cool and the precipitate of lead chlorofluoride filtered off, washed, dried and weighed.

3.1.4 Nitrogen Content

The organotin compound was decomposed by a Kjeldahl digestion and nitrogen determined by titration of the ammonia with standard hydrochloric acid.

3.1.5 Sulphur Content

An accurately weighed sample of sulphur-containing organotin compound (approximated 300 mg) was oxidized in a Parr bomb together with benzoic acid (300 mg), potassium perchlorate (1 g) and sodium peroxide (15 g). The residue was dissolved in water (100 ml), acidified with concentrated hydrochloric acid and treated with saturated bromine water (100 ml). On cooling, the solution was made neutral to methyl orange with sodium carbonate solution, 1N HCl added (1 ml) and the solution filtered hot through a No. 42 filter paper. The sulphate present was precipitated with barium chloride (5%), filtered, washed, ignited at 925°C. and weighed as barium sulphate.

3.2 Preparations

3.2.1 Tributyltin Saturated Carboxylates (Table 1)

Tributyltin acetate was prepared by the method of Luijten and van der Kerk (3), while tributyltin laurate was a commercial compound. Full details of the carboxylates prepared are given in Table 1. All organotin saturated aliphatic carboxylates were prepared by a similar procedure, and the methods described for the preparation of tributyltin formate and tributyltin isobutyrate are typical. Liquid carboxylates were purified by distillation under vacuum, or in the case of those with higher boiling points, by washing with petroleum ether (b.p., 40°-70°C.) at -60°C. Solid carboxylates were recrystallized from petroleum ether at -20°C., filtered and dried under vacuum at room temperature.

Tributyltin Formate. - Bis(tributyltin) oxide (59.6 g : 0.1 mole) and redistilled formic acid (9.2 g : 0.2 mole) were heated together on an oil bath at 110°C. for 0.5 hr. After drying under vacuum the crude material was distilled, b.p. 120-125°C/0.7 mm, n_D^{20} 1.4942, to give a 60% yield of the product. (Found: Sn, 35.2%. Calc. for $C_{13}H_{28}O_2Sn$:Sn, 35.5%.

Tributyltin Isobutyrate. - Bis(tributyltin) oxide (59.6 g : 0.1 mole) and isobutyric acid (17.6 g : 0.2 mole) were heated together on an oil bath at 110°C. for 0.5 hr., and the crude product then dried under vacuum (10-15 mm Hg press) at 70°C. for 1 hr., and then

distilled, b.p. 119°-122°C/2 mm. The solidified product was dissolved in petroleum ether (250 ml) and cooled overnight at -20°C. The crystals were removed, and dried under vacuum to give the product as fine white needles which had a m.p. of 49°C. The yield was 82%. (Found: Sn, 30.8% Calc. for $C_{16}H_{34}O_2Sn$:Sn, 31.5%).

3.2.2 Trialkyltin Unsaturated Carboxylates (Table 2)

The trialkyltin unsaturated carboxylates were prepared and purified by a procedure similar to that used for the preparation of the tributyltin saturated carboxylates, described in Section 3.2.1.

3.2.3 Trialkyltin Substituted Carboxylates (Table 3)

All the tributyltin substituted aliphatic carboxylates were prepared from bis(tributyltin) oxide and the appropriate substituted aliphatic acid. The preparation of tributyltin monochloroacetate is typical for this group of carboxylates.

Tributyltin Monochloroacetate. - Bis(tributyltin) oxide, b.p. 180°C/1.0 mm, η_D^{20} 1.4868 (59.6 g ; 0.1 mole) in a 250 ml round bottomed flask, was slowly treated at room temperature with recrystallized monochloroacetic acid (18.9 g ; 0.2 mole). The flask was then heated on an oil bath at 105° - 110°C. for 0.5 hr. to drive off water formed in the reaction. After drying under vacuum at 70°C. for 1 hr. the product was allowed to cool and solidify. The powdered solid was dissolved in petroleum ether (250 ml) and cooled overnight at -20°C. The filtered crystals were dried under vacuum to give the product as fine white needles, m.p. 46-47°C., in a yield of 72%. (Found: Sn, 30.3 ; Cl, 9.2%. Calc. for $C_{14}H_{29}ClO_2Sn$:Sn, 30.9; Cl, 9.3%).

Tributyltin dichloroacetate, trichloroacetate, hydroxyacetate, α-bromopropionate, β-bromopropionate, α-chloropropionate, phenylpropionate, bromoacetate and phenylacetate were all prepared by a method similar to that described above, and were recrystallized twice from petroleum ether.

Tributyltin pyruvate was obtained as a dark viscous liquid that decomposed when vacuum distillation was attempted. Tributyltin benzilate solidified on standing to a wax-like crude product. The product was refluxed with alcohol for 15 minutes, filtered, washed and dried at 105°C. to give fine white needles that decomposed when heated above 320°C.

3.2.4 Bis(tributyltin) Carboxylates (Table 4)

The bis(tributyltin) carboxylates were prepared from bis(tributyltin) oxide and the appropriate dicarboxylic acid. The carboxylates were obtained as white crystalline solids, insoluble in water and in many common organic solvents. In most cases the

he carboxylates were purified by recrystallization from hot so-octane.

Bis(tributyltin) oxalate. - Bis(tributyltin) oxide (59.6 g : 0.1 ole) and oxalic acid dihydrate (12.6 g : 0.1 mole) were heated ogether on an oil bath at 150°C. for 2 hr. When all the water iberated in the reaction had been removed the product was cooled nd allowed to stand for several days. The wax-like product was eated under reflux with petroleum ether (400 ml) and then iltered, to give the product as fine white insoluble needles, .p. 145° - 146°C., in a yield of 40%. (Found: Sn, 35.8%. alc. for $C_{26}H_{54}O_4Sn_2$:Sn, 35.5%).

Bis(tributyltin) sebacate. - Bis(tributyltin) oxide (59.6 g : .1 mole) and recrystallized sebacic acid (20.2 g : 0.1 mole) were eated together in an oil bath at 140°C. for 2 hr. On cooling he powdered solid was dissolved in iso-octane and recrystallized o give a 70% yield of product, with m.p. 101°C. (Found: Sn, 0.1%. Calc. for $C_{34}H_{70}O_4Sn_2$:Sn, 30.4%).

Bis(tributyltin) maleate. - Bis(tributyltin) oxide (59.6 g : .1 mole) and maleic acid (11.6 g : 0.1 mole) were heated together t 160°C. for 0.5 hr. and then at 180°C. for a further 0.5 hr. fter the water of reaction had been removed under vacuum the roduct was obtained as a viscous water-white liquid, with D^{20} 1.5100. Yield was 94%.

The liquid could not be distilled under vacuum. On standing or several days the product crystallized to a white powdery aterial, m.p. 42-43°C., that could not be recrystallized. Found: Sn, 33.9%. Calc. for $C_{28}H_{56}O_4Sn_2$:Sn, 34.2%).

Bis(tributyltin) malonate, succinate, adipate, pimelate, azelate nd fumerate were all purified by recrystallization from hot iso- ctane. Bis(tributyltin) tetrahydroxy adipate was insoluble in ll common organic solvents and was purified by washing with hot ater, drying, and then washing with hot iso-octane.

Bis(tributyltin) terephthalate. - Bis(tributyltin) oxide (59.6 g: .1 mole) and terephthalic acid (16.6 g : 0.1 mole) were heated ogether at 160° - 180°C. for 4 hr. After cooling the powdered roduct was heated under reflux three times with petroleum ether 200 ml) and filtered. The combined filtrates were evaporated own to 200 ml and allowed to stand overnight at 0°C. to crystal- ize. A white needle-like product, m.p. 78°C., was obtained. ield was 72%. (Found: Sn, 32.3%. Calc. for $C_{32}H_{52}O_4Sn_2$: Sn, 1.9%).

.2.5 Miscellaneous Organotin Carboxylates (Table 5)

Bis(tributyltin) carbonate. - Bis(tributyltin) oxide (29.8 g : .05 mole) was dissolved in 98% ethyl alcohol (200 ml) and carbon ioxide bubbled through the solution at room temperature for 12 hr. he solvent was removed under vacuum, while the liquid temperature

was kept below 50°C. The product was obtained as a pale viscous liquid, that solidified to a wax-like solid. Attempts to purify the material by distillation under vacuum caused decomposition and liberation of carbon dioxide. The product had η_D^{20} 1.4980, and the yield was 94%. (Found: Sn, 36.8%. Calc. for $C_{25}H_{54}O_3Sn_2$: Sn, 37.1%).

Tributyltin furoate and nicotinate were purified by recrystallization from petroleum ether.

Tributyltin α-naphthoate was soluble in alcohol, acetone and chlorinated hydrocarbons. It was recrystallized from petroleum ether at -20°C.

Tributyltin naphthalene-2-sulphonate was soluble in acetone and alcohol, but insoluble in petroleum ether and water. The crude reaction product was washed with petroleum ether and dried to yield a viscous oil which solidified to a wax-like product after 2-3 days.

Monobutyl (tributyltin) phthalate. - Bis(tributyltin) oxide (59.6 g : 0.1 mole) and monobutyl phthalate (44.4 g : 0.2 mole) were heated together on an oil bath at 110°C. for 0.5 hr. After drying under vacuum the crude material was distilled; b.p. 200°C/0.5 mm, η_D^{20} 1.5123. The yield was 84%. (Found: Sn 23.7%. Calc. for $C_{24}H_{40}Sn$: Sn, 23.2%).

A typical method for the preparation of dialkyl and diaryltin dicarboxylates is that used for dibutyltin dimethacrylate.

Dibutyltin dimethacrylate. - Dibutyltin oxide (24.9 g : 0.1 mole) prepared from commercial dibutyltin dichloride by the method described by Ingham and coworkers (1) was dispersed in toluene (200 ml) and refluxed for 3 hr. with redistilled, unstabilized methacrylic acid (17.2 g : 0.2 mole). On cooling any insoluble matter was filtered off and the filtrate concentrated under vacuum while the temperature of the reaction mixture was kept below 70°C. Attempts to distil the crude solid product under vacuum caused polymerization of the material. To retard polymerization, hydroquinone (0.04 g) was added and the crude material recrystallized from acetone. Sublimation under vacuum (1-2 mm Hg press) at 30°C. was used for final purification. A 72% yield of the sublimed product, m.p. 34°C. was obtained. (Found: Sn, 29.3%. Calc. for $C_{16}H_{28}O_4Sn$: Sn, 29.5%).

Polydioctyltin dimethacrylate. - Dioctyltin dimethacrylate prepared by the action of methacrylic acid on dioctyltin oxide, (Table 5), (51.5 g : 0.1 mole) was treated with benzoyl peroxide (0.515 g) and then heated at 140°C. for 1 hour. Polymerization took place almost immediately and on cooling the product was crushed to give a transparent friable powder, insoluble in most common solvents. The polymer, obtained in a yield of 98%, began to decompose when heated above 200°C. (Found: Sn, 22.8%. Calc. for $C_{24}H_{44}O_4Sn$: Sn, 23.0%).

.2.6 Miscellaneous Organotin Compounds (Table 6)

Butyltin oxide. - Butyltin trichloride, b.p. 90°C/0.2 mm, n_D^{20} 1.5233, (28.2 g : 0.1 mole) was dissolved in ether (200 ml) nd shaken at room temperature with a solution of sodium hydroxide 12.0 g : 0.3 mole) in water (100 ml).

The precipitated material was heated on a steam bath to remove he ether, and then filtered and washed. The crude material was hen stirred in boiling water (600 ml) for 1 hr., filtered, washed nd dried at 105°C. for 2 hr. Butyltin oxide was obtained as a hite, infusible, hygroscopic powder. Yield was 63%. (Found: n, 56.7%. Calc. for $C_4H_{10}O_2Sn$:Sn, 56.8%). This compound is lso called butyl stannonic acid.

Phenyltin oxide. - Phenyltin trichloride, b.p. 80°C/0.1 mm, n_D^{20} 1.5871, (30.25 g : 0.1 mole) was dissolved in ether and treated ith sodium hydroxide solution in the same manner as described bove. Phenyltin oxide was obtained as a white free-flowing owder, m.p. above 360°C., in a yield of 92%. (Found: Sn, 51.2%. alc. for $C_6H_6O_2Sn$:Sn, 51.9%).

Triphenyltin hydroxide. - Triphenyltin chloride, m.p. 107°C., 25.2 g : 0.066 mole) was dissolved in ethyl alcohol (300 ml) and reated with a solution of sodium hydroxide (3.0 g) in 80% ethyl lcohol (90 ml). After refluxing for 20 mins. the precipitated odium chloride was removed by filtration and the hot filtrate reated with water until a faint turbidity was obtained. The ooled solution was then stored at 0°C. for 16 hr. to allow the roduct to crystallize. The crystals were filtered, washed and ried at 70°C. to give a product, with m.p. 124°C. Yield was 90%. Found: Sn, 33.1%. Calc. for $C_{18}H_{16}OSn$:Sn, 32.4%).

On heating triphenyltin hydroxide to above its melting point, ater was eliminated and bis(triphenyltin) oxide, a hygroscopic aterial was formed.

Dioctyltin dihydride. - Powdered lithium aluminium hydride 5.7 g : 0.15 mole) was suspended in anhydrous diethyl ether 250 ml) under a nitrogen atmosphere. Dioctyltin dichloride, m.p. 8°C., (42.7 g : 0.3 mole) in ether (100 ml) was added dropwise to he stirred solution, and the reaction mixture then refluxed for .5 hr. On cooling hydroquinone (0.5 g) was added followed by ater (12 ml) to decompose the reaction complex. After the ddition of a 20% aqueous solution of sodium potassium tartrate 300 ml) the product was filtered and the filtrate dried over nhydrous sodium sulphate. The ether was removed under vacuum and he product recovered by distillation at 110° - 112°C/0.2 mm, had n_D^{20} 1.4774. The yield was 45%. Repeated distillation caused ecomposition and stannous oxide was formed in the distillation lask. Although no chlorine could be detected in the final pro- uct, the purity of the material is reflected in the analytical igures. (Found: Sn, 32.9%. Calc. for $C_{16}H_{36}Sn$:Sn, 34.2%).

Triphenyltin fluoride. - Anhydrous ammonium fluoride, dried azeotropically with carbon tetrachloride, (5.5 g : 0.15 mole) was suspended in anhydrous ethyl alcohol (200 ml) and treated under reflux with a solution of triphenyltin chloride (38.5 g : 0.1 mole) in ethyl alcohol (200 ml). After refluxing for 1 hr. the hot solution was filtered and the white insoluble product washed with hot water until no chloride ions could be detected in the washings. The product after washing with acetone and drying at 60°C., was obtained in a yield of 93%. The white insoluble material decomposed when heated above 360°C. (Found: Sn, 31.9; F, 5.1%. Calc. for $C_{18}H_{15}FSn$:Sn, 32.2; F, 5.2%).

Tributyltin fluoride. - Tributyltin chloride, b.p. 146°C/4 mm, η_D^{20} 1.4922, (32.5 g : 0.1 mole) was treated with anhydrous ammonium fluoride (7.4 g : 0.2 mole) and heated with occasional stirring in an oil bath at 120°C. for 1 hr. On cooling the solid product was powdered and washed on a filter with hot water until free from chloride ions. The product was obtained as fine white needles by recrystallization from methyl alcohol (600 ml). It had m.p. 218° - 219°C., and the yield was 90%. (Found: Sn, 38.1 ; F, 6.1%. Calc. for $C_{12}H_{27}FSn$:Sn, 38.4; F, 6.2%).

Tributyltin fluoride may also be obtained in good yields by the reaction of ammonium fluoride on bis(tributyltin) oxide.

Tributyltin isothiocyanate. - Tributyltin chloride (65.2 g : 0.2 mole) was dissolved in 95% ethyl alcohol (200 ml) and treated with a solution of potassium thiocyanate (24.3 g) in 50 ml of the same solvent. After heating under reflux for 2 hr. the solution was cooled and the precipitated potassium chloride removed by filtration. The solvent was removed under vacuum, and the residue dissolved in ether (200 ml), washed twice with water and dried. Fractionation gave tributyltin isothiocyanate, b.p. 146°C/0.2 mm, η_D^{20} 1.5432, in a yield of 91%. (Found: Sn, 34.0; S, 9.1; N, 4.0%; Calc. for $C_{13}H_{27}NS$ Sn:Sn, 34.1, S, 9.2; N, 4.0%).

Tributyltin succinimide. - Bis(tributyltin) oxide (59.6 g : 0.1 mole) and succinimide (19.8 g : 0.2 mole) were heated together for 1 hr. at 160°C. The water liberated was removed under vacuum and the product distilled, b.p. 144°C/0.2 mm. The yield was 79% and the product had, η_D^{20} 1.5086, m.p. 21°C. (Found: Sn, 30.4; N, 3.6%. Calc. for $C_{16}H_{31}NO_2Sn$:Sn 30.6; N, 3.6%).

Tributyltin phthalimide. - Bis(tributyltin) oxide (59.6 g : 0.1 mole) and phthalimide (29.4 g : 0.2 mole) were heated under reflux in a Dean and Starks apparatus with 100 ml of toluene. When all the water from the reaction had separated (2 hr.) the toluene was removed under vacuum and the product distilled, b.p. 194 - 195°C/1.0 mm. The yield was 82% and the product had η_D^{20} 1.5412. (Found: Sn, 27.0; N, 3.2%. Calc. for $C_{20}H_{31}NO_2Sn$:Sn, 27.2; N, 3.2%).

Butyltin trichloride dipyridinate. - Butyltin trichloride 14.15 g : 0.05 mole) was added slowly to redistilled pyridine 11.85 g : 0.15 mole), care being taken to avoid overheating due o the vigorous exothermic reaction between the reactants. After he addition the materials were heated on an oil bath at 120°C. or 10 mins, cooled and the white solid crushed to a powder. fter washing the powder twice with petroleum ether to remove any nreacted pyridine, the product was recrystallized from acetone. he product, butyltin trichloride dipyridinate had m.p. 119°C. ield was 85%. (Found: Sn, 27.0; Cl, 23.9; N, 5.9%. Calc. for $_{14}H_{19}Cl_3N_2Sn$:Sn, 27.0; Cl, 24.2; N, 6.4%).

Tributyltin nitrate. - Tributyltin chloride (32.6 g : 0.1 mole) as slowly added dropwise to a stirred solution of silver nitrate 17.0 g : 0.1 mole) in ethyl alcohol (350 ml) at room temperature. he solution was refluxed for 1 hr., cooled, filtered and the olvent removed under vacuum. The product was obtained by dis- illation, b.p. 156 - 157°C/1.0 mm, η_D^{20} 1.4971. Yield, 72%. Found: Sn, 33.5; N, 3.8%. Calc. for $C_{12}H_{27}NO_3Sn$:Sn, 33.8; , 4.0%).

4. ACKNOWLEDGEMENT

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5. REFERENCES

1. Ingham, R.K., Rosenberg, S.D., and Gilman, H. 1960. Chem. Reviews, 60, 459.

2. Neumann, W.P. 1963. Angew. Chem., 2, 165.

3. Luijten, J.G.A., and van der Kerk, G.J.M. 1955. "Investigations in the Field of Organotin Chemistry", Tin Research Institute, England.

4. Noltes, J.G., and van der Kerk, G.J.M. 1958. "Functionally Substituted Organotin Compounds", Tin Research Institute, England.

5. Alleston, D.L., and Davies, A.L. 1962. J. Chem. Soc., 2050.

6. Montermoso, J.C., Andrews, T.M., and Marinelli, L.P. 1958. J. Poly. Sci., 32, 523.

7. West, R., Baney, R.H., and Powell, D.L. 1960. J. Amer. Chem. Soc., 82, 6270.

8. Poller, R.C. 1962. J. Inorg. Nucl. Chem. 24, 593.

9. Friebe, E., and Kelker, H. 1963. Z. analyt. Chem., 192, 267.

10. van der Kerk, G.J.M., Luijten, J.G.A., and Janssen, M.J. 1962. Chimia, 16, 10.

11. Luijten, J.G.A., Janssen, M.J., and van der Kerk, G.J.M. 1962. Rec. trav. chim., 81, 202.

12. Abel, E.W., Brady, D., and Lerwill, B.R. 1962. Chem. and Ind., 1333.

13. Pfeiffer, P., Friedmann, B., Lehnardt, R., Luftensteiner, H., Prade, R., and Schnurmann, K. 1911. Z. anorg. Chem., 71, 97.

14. Shapiro, P.J., and Becker, E.I. 1962. J. Org. Chem., 27, 4668.

TRIBUTYLTIN SATURATED CARBOXYLATES

Compound	Yield %	Melting Point °C	Boiling Point °C/mm	ηD^{20}	Sn, Calc. %	Sn, Found %
Tributyltin formate*	60	-	120-125/0.7	1.4942	35.5	35.2
Tributyltin acetate	80	84.5	-	-	34.0	34.2
Tributyltin propionate	82	69-70	-	-	32.7	33.1
Tributyltin butyrate	87	67-68	-	-	31.5	31.6
Tributyltin isobutyrate*	82	49	119-122/2.0	-	31.5	30.8
Tributyltin valerate	85	61-62	-	-	30.4	30.6
Tributyltin isovalerate	79	67-68	-	-	30.4	30.5
Tributyltin caproate	82	47	-	-	29.3	29.1
Tributyltin isocaproate	81	65-66	-	-	29.3	29.2
Tributyltin heptylate	80	55-56	-	-	28.3	28.6
Tributyltin caprylate	80	45-47	-	-	27.4	26.7
Tributyltin pelargonate	80	43-44	-	-	26.6	26.3
Tributyltin caprate	80	-	160-161/2.0	1.4815	25.7	25.5
Tributyltin undecanoate	80	-	167-169/2.0	1.4801	25.0	24.8
Tributyltin laurate	80	14-15	180-185/2.0	1.4825	24.3	24.2
Tributyltin tridecylate	80	-	-	1.4785	23.6	23.2
Tributyltin myristate	80	-	-	1.4792	23.0	23.1
Tributyltin pentadecylate	80	-	-	1.4782	22.4	22.5
Tributyltin palmitate	80	-	-	1.4798	21.8	21.6
Tributyltin margarate	80	-	-	1.4774	21.2	21.1
Tributyltin stearate	80	18.23	-	1.4778	20.7	20.6

* See Experimental Section 3.2.1

TABLE 2

TRIALKYLTIN UNSATURATED CARBOXYLATES

Compound	Yield %	Melting Point °C	Boiling Point °C	η_D^{20}	Sn, Calc. %	Sn, Found %
Tributyltin crotonate	84	82	-	-	31.7	31.4
Tributyltin oleate	78	-	-	1.4836	20.8	19.5
Tributyltin linoleate	82	-	-	1.4914	20.8	20.7
Tributyltin undecylenate	87	17	-	1.4850	25.1	24.4
Tributyltin ricinoleate	72	-	-	1.4904	20.2	20.0
Tributyltin cinnamate	63	69-70	-	-	27.2	27.2
Trioctyltin acrylate	92	44-45	-	-	22.4	22.1

TRIALKYLTIN SUBSTITUTED CARBOXYLATES

Compound	Yield %	Melting Point °C	Boiling Point °C/mm	n_D^{20}	Sn, Calc.	Sn, Found %	Cl, Calc. %	Cl, Found %
Tributyltin monochloroacetate*	72	46-47	-	-	30.9	30.3	9.3	9.2
Tributyltin dichloroacetate	78	50-51	-	-	28.3	27.5	16.9	17.1
Tributyltin trichloroacetate	73	80.5	-	-	26.1	25.9	23.5	23.9
Tributyltin hydroxyacetate	70	75-76	-	-	32.6	33.1	-	-
Tributyltin α-bromopropionate	68	69-70	-	-	27.0	27.2	-	-
Tributyltin β-bromopropionate	74	61-62	-	-	27.0	27.5	-	-
Tributyltin α-chloropropionate	91	59-60	-	-	29.9	30.4	-	-
Tributyltin α-hydroxypropionate	68	-	130/0.7	1.4730	31.3	31.0	-	-
Tributyltin phenylpropionate	64	65	-	-	27.0	26.5	-	-
Tributyltin pyruvate*	87	-	Decomp.	1.5040	31.5	31.2	-	-
Tributyltin bromoacetate	89	52-53	-	-	27.8	28.4	-	-
Tributyltin phenylacetate	83	61-62	-	-	27.9	28.4	-	-
Tributyltin benzilate*	72	Decomp. 320	-	-	23.0	25.1	-	-

* See Experimental Section 3.2.3

TABLE 4

BIS(TRIBUTYLTIN) CARBOXYLATES

	Yield %	Melting Point °C	Sn, Calc. %	Sn, Found %
Bis(tributyltin) oxalate*	40	145-146	35.5	35.8
Bis(tributyltin) malonate	82	86-87	34.8	34.5
Bis(tributyltin) succinate	84	91-93	33.9	33.9
Bis(tributyltin) adipate	78	105	32.8	32.6
Bis(tributyltin) pimelate	81	101	32.2	33.0
Bis(tributyltin) azelate	80	100	31.0	30.9
Bis(tributyltin) sebacate*	70	101	30.4	30.1
Bis(tributyltin) maleate*	94	42-43	34.2	33.9
Bis(tributyltin) fumarate	80	128	34.2	34.1
Bis(tributyltin) tetra-hydroxy adipate	80	decomp. over 200	30.1	30.4
Bis(tributyltin) * terephthalate	72	78	31.9	32.3
Bis(tributyltin) phthalate	94	decomp. liquid, η_D^{20} 1.5234	31.9	31.7

* See Experimental Section, 3.2.4

TABLE 5

MISCELLANEOUS ORGANOTIN CARBOXYLATES

Compound	Yield %	Melting Point °C	Boiling Point °C	η_D^{20}	Sn, Calc. %	Sn, Found %
Bis(tributyltin) carbonate *	95	-	decomposes	1.4980	37.1	36.8
Tributyltin furoate	92	86-87	-	-	29.6	29.1
Tributyltin α-naphthoate	87	32	-	-	25.7	25.4
Tributyltin nicotinate	82	70	-	-	28.8	28.9
Tributyltin naphthalene-2-sulphonate	70	40-45	-	-	23.9	23.5
Monomethyl(tributyltin) phthalate	87	38	180-184/ 0.4 mm	-	25.3	25.0
Monobutyl(tributyltin) * phthalate	87	-	200/0.5 mm	1.5121	23.2	23.7
Dibutyltin dimethacrylate*	72	34	-	-	29.5	29.3
Dioctyltin dimethacrylate	81	-	decomposes	1.4860	23.0	22.9
Polydioctyltin diacrylate	97	decomp. 200	-	-	24.4	24.1
Polydioctyltin dimethacrylate*	98	decomp. 200	-	-	23.0	22.8

* See Experimental Section 3.2.5

MISCELLANEOUS ORGANOTIN COMPOUNDS

Compound	Yield %	Melting Point °C	Boiling Point °C/mm	ηD^{20}	Sn, Calc. %	Sn, Found %	Calc. %	Found %	N, Calc. %	N, Found %
Butyltin oxide*	63	>350	-	-	56.8	56.7	-	-	-	-
Phenyltin oxide*	92	>350	-	-	51.9	51.2	-	-	-	-
Triphenyltin hydroxide*	90	124	-	-	32.4	33.1	-	-	-	-
Dioctyltin dihydride*	45	-	110-112/0.2	1.4774	34.2	32.9	-	-	-	-
Diphenyltin difluoride	76	360	-	-	38.3	38.0	-	-	-	-
Triphenyltin fluoride*	93	360	-	-	32.2	31.9	F, 5.2	F, 5.1	-	-
Tributyltin fluoride*	90	218-219	-	-	38.4	38.1	F, 6.2	F, 6.1	-	-
Tributyltin isothiocyanate*	91	-	146/0.2	1.5432	34.1	34.0	S, 9.2	S, 9.1	4.0	4.0
Tributyltin succinimide*	79	21	144/0.2	1.5086	30.6	30.4	-	-	3.6	3.6
Tributyltin phthalimide*	82	-	194-195/1.0	1.5412	27.2	27.0	-	-	3.2	3.2
Butyltin trichloride dipyridinate*	85	119	-	-	27.0	27.0	Cl, 24.2	Cl, 23.9	6.4	5.9
Dibutyltin dichloride dipyridinate	92	65-66	-	-	-	-	-	-	-	-
Tributyltin chloride monopyridinate	95	-	decomp.	1.5174	29.3	29.1	-	-	-	-
Tributyltin nitrate*	62	-	154-156/1	1.4955	33.8	33.5	-	-	-	-

* See Experimental Section 3.2.6

APPENDIX 10 INFRARED STUDIES ON ORGANOTIN COMPOUNDS

10a	The Infrared Spectra of Organotin Compounds R.A. CUMMINS and P. DUNN Report 266. Defence Standards Laboratories, Department of Supply, Melbourne, Victoria	10.2 - 10.33
10b	Sadtler Infrared Spectra of Organotin Compounds. 1966. Four spectra as examples	10.34 - 10.36
10c	Organotin Carboxylates R.A. CUMMINS and P. DUNN *Aust. J. Chem.*, 17, No. 2, 185-91 (1964)	10.37 - 10.44
10d	Preparation, Properties and Structure of Some Organotin Acrylates. R.A. CUMMINS, P. DUNN and D. OLDFIELD *Aust. J. Chem.*, 24, No. 11, 2257-66 (1971)	10.45 - 10.55
10e	Tributyltin Isothiocyanate and Isocyanide R.A. CUMMINS and P. DUNN *Aust. J. Chem.*, 17, No. 4, 411-18 (1964)	10.56 - 10.64
10f	Some Reactions of Organotin Azides P. DUNN and D. OLDFIELD *Aust. J. Chem.*, 24, No. 3, 645-7 (1971)	10.65 - 10.69

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REPORT 266

THE INFRARED SPECTRA OF ORGANOTIN COMPOUNDS

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SUMMARY

The infrared spectra of organotin compounds are reviewed, and assignments listed for infrared vibrations involving the tin atom combined with other atoms. A bibliography of organotin compounds on which some infrared data have been published is given.

The infrared spectra of 198 organotin compounds of which 41 were commercial products have been recorded over the frequency range 4000-450 cm^{-1}. About half of the compounds examined were new materials.

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THE INFRARED SPECTRA OF ORGANOTIN COMPOUNDS

1. LITERATURE SURVEY

Although well over 800 organotin compounds are known (1), only about 100 compounds have been studied by infrared techniques, and of these, only tetramethyltin, has been studied in detail.

1.1 Organotin Hydrocarbons

The infrared and Raman spectra of tetramethyltin have been studied by various workers (2-8), but there is considerable disagreement about the interpretation of the spectra. In general the frequency assignments of Lippincott and Tobin (7) agree with those of Young, Koehler and McKinney (4), but more recent work by Edgell and Ward (8) has shown that differences in assignments exist at frequencies above 2000 cm^{-1}. At frequencies below this there is general agreement except for the presence of small bands due to impurities.

The tetramethyltin molecule like other tetramethyl compounds of Group IV elements appears to have tetrahedral symmetry, and, on this basis, Edgell and Ward (8) have calculated the number of fundamental infrared vibrations of this molecule and assigned most of the bands found in the spectrum. The strong band at 1445 cm^{-1} is due to the CH_3 asymmetric deformation vibration while the band at 1190 cm^{-1} is assigned to the CH_3 symmetric deformation vibration.

All workers assign the band near 530 cm^{-1} to the $Sn-CH_3$ asymmetric stretching vibration. In tetramethyltin a very strong infrared band is found at 764 cm^{-1} which is assigned to the $Sn-CH_3$ rocking vibration. As shown in Table 1 this band appears at 800-750 cm^{-1} in the spectrum of many methyltin compounds. Waters and Woodward (9) examined the Raman spectra in the vapour state of the tetramethyl compounds of carbon, silicon, germanium, tin and lead. The bands near 780 cm^{-1} and 1200 cm^{-1} are assigned to the methyl rocking and to the methyl symmetric deformation vibrations respectively.

Dillard and Lawson (10) examined the infrared and Raman spectra of some tin alkyls and made assignments of some skeletal frequencies on the basis of assumed symmetries.

The vinyl derivatives of the elements of Groups III and IV can be identified by a weak band in the region 2000-1850 cm^{-1} (11), and tetravinyltin when examined as a liquid smear shows this band near 1908 cm^{-1}.

Spectroscopic data by Noltes and van der Kerk (12) was used to confirm the formation of 1, 2-bis-(triphenyltin) ethane from triphenyltin hydride and triphenylvinyltin. Similarly Leavitt and Matternas (13) used infrared data to determine the structure of organotin compounds formed by the addition of organotin hydrides to diacetylenic compounds.

Noltes and co-workers (14,15,16) state that aromatic compounds of the Group IV elements can be characterized by certain infrared bands. In the case of phenyltin compounds, a band near 1070 cm^{-1} is independent of the number of phenyl groups attached to the tin atom, and is claimed to be missing in the aliphatic tin compounds. Bands in the 1070 cm^{-1} region have been used to characterize compounds such as 1-triphenylstannyl-2-triphenylsilyl ethane and the corresponding germane compounds. However, as shown in our spectra, propyltin and butyltin compounds also have absorption bands in the 1070 cm^{-1} region and the use of this region to unambiguously characterize phenyltin compounds could be misleading.

Further infrared studies on the phenyl derivatives of carbon, germanium, silicon, tin and lead have been carried out by West, Baney and Powell (17) and by Margoshes and Fassel (18).

Harrah, Ryan and Tamborski (19) studied the spectra of phenyltin compounds in the 4000-300 cm^{-1} region. They showed that the spectra in the 4000-650 cm^{-1} region are characteristic of a monosubstituted benzene compound, but are not sufficiently characteristic for the qualitative identification of phenyltin compounds. They further showed however, that the spectra of phenyltin compounds in the 650-300 cm^{-1} region are quite distinctive and can be used for their identification.

The spectrum of hexaphenylditin is similar to that of tetraphenyltin, and the Sn-Sn axial deformation frequency has been calculated to occur near 188 cm^{-1} (19). The spectra of mixed metal compounds such as triphenyltin triphenyl germane show band splitting as well as extra small bands not present in ditin compounds. These bands are assumed to be due to tin-germanium vibrations which are infrared active.

Recently Poller (20) investigated twenty phenyltin compounds in the 4000-670 cm^{-1} region, and assigned frequencies for some of the vibrations.

Braye, Hübel and Caplier (21) report the spectra of two complex tin hydrocarbons, hexaphenylstannole and octaphenyl-5-stanna-spiro (4,4) nona-1, 3, 6, 8-tetraene prepared from 1,4 dilithio-tetraphenyl butadiene and tin halide.

1.2 Organotin Oxides

Poller (20), Friebe and Kelker (22), and Kushlefsky, Simmons, and Ross (23) have studied the structure of triphenyltin hydroxide and bis-(triphenyltin) oxide by infrared techniques. The

stretching frequency of the Sn-O group has been calculated as about 570 cm^{-1}, which is in good agreement with the range 643-580 cm^{-1} reported by Brown, Okawara and Rochow (24) for methyltin compounds containing the Sn-O-Sn group. In certain trisubstituted organotin hydroxides and oxides bands assigned to the Sn-O vibration occur in the region 900-750 cm^{-1}. Poller (20) suggested that in these compounds overlap occurs between the oxygen p-orbitals and the d-orbitals of the tin atom. The resulting higher bond order would cause an increase in the force constant leading to a higher vibration frequency. In the case of the phenyltin compounds, the characteristic band at 777 cm^{-1} for bis-(triphenyltin) oxide and at 912 and 898 cm^{-1} for triphenyltin hydroxide can be used to distinguish between these compounds (20). Poller (25) has also shown that a band at 828 cm^{-1} in bis-(tri-o-phenoxyphenyltin) oxide can be assigned to vibrations of the Sn-O-Sn group.

1.3 Organotin Carboxylates

Several workers have studied the structure of the methyltin carboxylates using infrared techniques, and have proposed configurations for the trimethyl and the dimethyltin groups. Okawara, Webster and Rochow (26) examined trimethyltin carboxylates and halides over the range 3500-400 cm^{-1}, and compared the carboxylate spectra with those of the methyl silicon carboxylates. Whereas the latter were similar to esters, the spectra of the methyltin carboxylates indicated the presence of a carboxylate ion. Freeman (27) has also shown that dibutyltin diacetate shows carboxyl absorption near 1580 cm^{-1} which is typical of acetate salts. Also Okawara and Sato (28) have assigned bands in trimethyltin formate, acetate and monochloroacetate to the asymmetric and symmetric vibration of the carboxylate ion.

With trimethyltin carboxylates Okawara and co-workers (26,28) interpret the spectra as being superpositions of the absorptions of the carboxylate anion and the trimethyltin cation since in the the methyltin acetates two bands remained after assigning the bands characteristic of the acetate ion.

Recently Beattie and Gilson (29) have given an alternative interpretation of the spectra of the organotin carboxylates, and have suggested that these compounds may exist as chelate compounds involving a 5 - coordinated tin atom. Luijten, Janssen and van der Kerk (30,31) suggest an associated structure for compounds like trioctyltin acetate when in solution or as a liquid melt. No great differences would be expected between the spectra of ionic carboxyl compounds and compounds containing chelate or bridging carboxyl groups.

Poller (20) also studied the carboxyl stretching frequency of organotin carboxylates, but was unable to distinguish between an ionic and a covalent structure.

However Janssen, Luijten and van der Kerk (32), having completed their study of the structure of the trialkyltin acylates, have

shown that in the solid state these compounds occur as co-ordination polymers in which each tin atom is 5 - coordinated, for example, by three alkyl groups. In non-polar solvents the compounds were shown to be mono molecular and to resemble organic esters. From a study of a different series of compounds to those examined by Janssen and coworkers (32) we have been able to confirm their findings on the structure of the organotin carboxylates.

1.4 Organotin Hydrides

From a study of organotin hydrides, Mathis-Noel, Lesbre and Sérée de Roch (33) showed that monohydrides have a characteristic absorption near 1820 cm^{-1}, while dihydrides absorb near 1835 cm^{-1}. With the corresponding silane hydrides, the absorption is between 2150 and 2100 cm^{-1}.

Behnke and Tamborski (34) have assigned a band at 565 cm^{-1} in the spectrum of triphenyltin hydride to the Sn-H deformation vibration. Between 1500 and 700 cm^{-1} the spectra of dialkyltin dihydrides and trialkyltin hydrides are similar for the same alkyl groups, and similar to the spectra of the corresponding organotin chlorides.

1.5 Organotin Halides

Domange and Guy (35) studied the infrared spectra of diethyltin di-iodide, triethyltin iodide and triethyltin hydroxide, and showed that characteristic bands near 1230, 1178 and 1021 cm^{-1} can be used to determine the presence of less than 10% of the mono-iodide in the di-iodide.

Behnke and Tamborski (34) have assigned bands at 327 cm^{-1} and 225 cm^{-1} in the spectra of triphenyltin chloride and triphenyltin bromide respectively to the Sn-halogen stretching vibration.

A study of perfluoromethyltin compounds has been made by Kaesz, Phillips and Stone (36), who have shown that C-F groups in organotin compounds give bands near 1158 and 1073 cm^{-1}. Trimethylperfluoromethyltin shows other bands near 790 and 730 cm^{-1} which are characteristic methyl rocking modes. In this compound the bands due to C-F groups are more numerous than in the perfluoromethyltin compound, and the C-C stretching vibration is characterized by a band at 935 cm^{-1} which has been used to distinguish this compound from triphenylperfluoromethyltin.

1.6 Miscellaneous

Both Brown, Okawara and Rochow (24) and Poller (20) suggest that vibrations connected with the Sn-S-Sn and the Sn-Cl bonds occur at frequencies below 400 cm^{-1}.

Seyferth and Kahlen (37) reported that trimethyltin (iso) cyanide shows one band in the C≡N region near 2175 cm^{-1} but none in the isocyanide region. The location of this infrared band does not permit a distinction between a covalent and a highly polar cyanide.

The infrared spectra of addition compounds of tin tetrachloride in the caesium bromide region have been reported by Beattie, McQuillan, Rule and Webster (38), and Kida and coworkers (39) have made similar observations on tin tetrabromide di(pyridine N-oxide). Also Brown and Kubota (40) reported the frequency and intensity of the nitrile band of the tin tetrachloride-benzonitrile complex and the low frequency (725-600 cm^{-1}) spectra of the solid tin tetrachloride-bis-acetonitrile and tin tetrachloride-bis-p-methoxybenzonitrile. Sharp and Sheppard (41) report the addition compound of tin tetrachloride and triphenyl methyl chloride as an ionic compound with triphenylmethyl as cation. Smithson and Matta (42) have reported the spectra of dibutyltin bis-(2 mercaptobenzthiazole) and of stannous octanoate and stannous caprate.

Several workers have followed organotin reactions by infrared techniques. Noltes and van der Kerk (43) showed that dipropyl-2(-phenylvinyl) tin hydride is formed by the reaction of dipropyltin dihydride and phenyl acetylene. The characteristic Sn-H stretching vibration at 1824 cm^{-1}, the C=C stretching vibration at 1596 cm^{-1} and the C-H bending vibration of trans disubstituted ethylenes at 988 cm^{-1} in the spectrum of the product confirms the reaction.

Van der Kerk, Luijten and Noltes (44) confirmed the formation of triphenylcyanoethyltin from triphenyltin hydride and acrylonitrile by comparing the infrared spectrum to that of triphenylcyanomethyltin. Both spectra were similar in the region 1650-1350 cm^{-1} and showed the absence of free methyl groups. Also both compounds showed a relatively weak band near 2250 cm^{-1}.

1.7 Conformation and the Tin-Carbon Bond

In trimethyltin and dimethyltin halides (except fluorides) two bands near 500 and 550 cm^{-1} have been assigned to the symmetric and asymmetric Sn-CH_3 stretching vibrations (26). If the trimethyltin group was planar only one band near 550 cm^{-1} would be expected, and the absence of the band at 500 cm^{-1} in trimethyltin fluoride and carboxylates has been used to indicate the presence of planar trimethyltin groups in these compounds. Similarly the absence of the 500 cm^{-1} vibration in dimethyltin carboxylates has been used to assign a linear structure to the dimethyltin group (26).

The presence of planar trimethyltin groups in compounds such as trimethyltin hydride and halides has been proposed by Kreigsmann and Pitschschan (45). Trimethyltin fluoride is different from other halides in that it forms an ionic lattice (26,29). With trimethyltin chloride and bromide association is proposed involving tin-halogen-tin bridges (26).

New organotin compounds (containing tin-nitrogen bonds) of the type R_3SnR^1, where R^1 is an unsaturated group containing two nitrogen atoms in the 1:3 position have been studied by Luijten and co-workers (30,31). On the basis of the absence of the band near 500 cm^{-1} they postulate a planar R_3Sn group, where the second nitrogen in the R^1 groups is co-ordinated intermolecularly with another tin atom. This 5 - coordinate tin concept has also been proposed by Beattie, McQuillan and Hulme (46) for the structure of trimethyltin chloride pyridinate.

Similar work has been undertaken by Okawara, Hathaway and Webster (47) who have examined the infrared spectra of trimethyltin perchlorate, nitrate and carbonate in the solid state. The spectra obtained were inconsistent with the spectra of free anions but indicated the presence of covalently bonded groups and this suggested the presence of 5 - coordinate tin in the solid state. In the nitrate and carbonate compounds, two Sn-C stretching frequencies occur indicating that the trimethyltin group is not planar in these compounds.

The infrared spectrum of trimethyltin tetrafluoroborate has been studied by Hathaway and Webster (48) who suggest that covalent bonding through two of the fluorine atoms can occur. In this case the tetrafluoroborate group forms a bridge between separate trimethyltin residues to give a chain structure involving a 5 - coordinate tin atom.

Band assignments and a bibliography of organotin compounds on which infrared data have been reported are given in Tables I, II and III.

2. DETAILS OF SPECTRA

The infrared spectra of 198 organotin compounds, of which 41 were commercial products, have been recorded at Defence Standards Laboratories over the **frequency** range 4000-450 cm^{-1}. About half of the compounds examined were new compounds prepared at D.S.L.

All the spectra were recorded on a Perkin-Elmer Model 125 spectrometer using a spectral slit width of about 2 cm^{-1}. Details of the spectra and the sample form are listed in Sections 6.1 - 6.13.

Some general comments on the recorded spectra are as follows:-

2.1 Organotin Carboxylates

All the solid carboxylates investigated exhibit a strong band in the region near 1570 cm^{-1}. This band corresponds to the asymmetric stretching frequency of the carboxylate ion. As mentioned earlier however (Section 1.3) it could also be due to a chelated group.

On melting, this band shifts to the region of 1640 cm^{-1}, a shift that would appear to be too large to be accounted for by a change of state. A more reasonable explanation is that the compounds when in the liquid state have an ester-like configuration. This is supported both by the shape of the band which becomes much more like a normal C=O band and also by the fact that all these compounds when in solution in non-polar solvents exhibit only one band, and that near 1640 cm^{-1}.

It is noticeable that all the liquid carboxylates, with the exception of the formate, exhibit both bands. No mesophase could be detected and thus liquid crystallinity is unlikely. On heating these carboxylates to about 70°C the bands near 1550 cm^{-1} vanish and those near 1640 cm^{-1} increase in intensity.

It would appear that organotin carboxylates in the solid state are chelated to the tin atom, while in liquid compounds an equilibrium between the chelated state and the covalent ester state is possible unless disturbed either by heat or by solution.

2.2 Organotin Oxides

The trialkyltin oxides and bis-(triphenyltin) oxide exhibit a strong band near 770 cm^{-1} which disappears during any reaction involving the oxygen atom and is probably due therefore to a stretching vibration of tin and oxygen.

All the mono-substituted and di-substituted oxides studied exhibit a strong band near 550 cm^{-1} which disappears on reaction and hence must also be associated with a tin-oxygen stretching mode.

Attempts to prepare trialkyltin hydroxides were unsuccessful. Triphenyltin hydroxide however is stable at room temperatures and exhibits a strong band near 3620 cm^{-1}, and a strong doublet near 910 cm^{-1} and 894 cm^{-1}. Deuteration shifts these bands to 2669 cm^{-1} and 673 cm^{-1} respectively. It seems likely that these bands are associated with an OH stretching and an OH deformation frequency, and our observations are in excellent agreement with those of Friebe and Kelker (22).

Apart from triphenyltin hydroxide only the mono-substituted oxides (stannonic acids) exhibit bands due to hydroxyl groups, and in these compounds there is evidence for the existence of co-ordinated water.

It has been found that trisubstituted oxides may have the oxygen atom replaced by sulphur, merely by dissolving the compound in carbon disulphide. In this replacement reaction the triaryltin oxides react much more slowly than the trialkyltin oxides.

2.3 Organotin Hydrides

All hydrides exhibit a very strong band in the region 1835-1800 cm^{-1}, and there is no evidence of band splitting in the dihydrides. Using Linnett's equations (49) and assuming a tetrahedral configuration it can be shown that the separation between a symmetric and an asymmetric frequency would be of the order of 10 cm^{-1} and hence the bands would be unresolved.

2.4 Organotin Fluorides

All the difluorides as well as the trifluoride exhibit evidence of water which could be co-ordinated. The existence of tin-fluorine bands which would be expected in the 600-500 cm^{-1} region is inconclusive.

2.5 Organotin Chlorides

An interesting feature of the spectra of the chlorides is found in the butyl series, where, starting with tetrabutyltin, the alkyl groups are successively substituted with chlorine down to monobutyltin trichloride. In this series, while most of the bands associated with the butyl group, such as the methyl symmetric deformation near 1370 cm^{-1} and another strong band near 1070 cm^{-1} are diminishing in intensity three bands between 1250 and 1150 cm^{-1} are increasing.

This behaviour is also present in both the propyl and the octyl series, although in the latter the bands are considerably weaker. Figure 1 shows plots of the extinction coefficient versus the number of alkyl groups for two bands in a series of butyl and propyltin compounds, respectively.

It is believed that the behaviour of the bands that are increasing in intensity is due to a field effect of the halogen atoms on wagging and/or twisting modes of the α-methylene group(s).

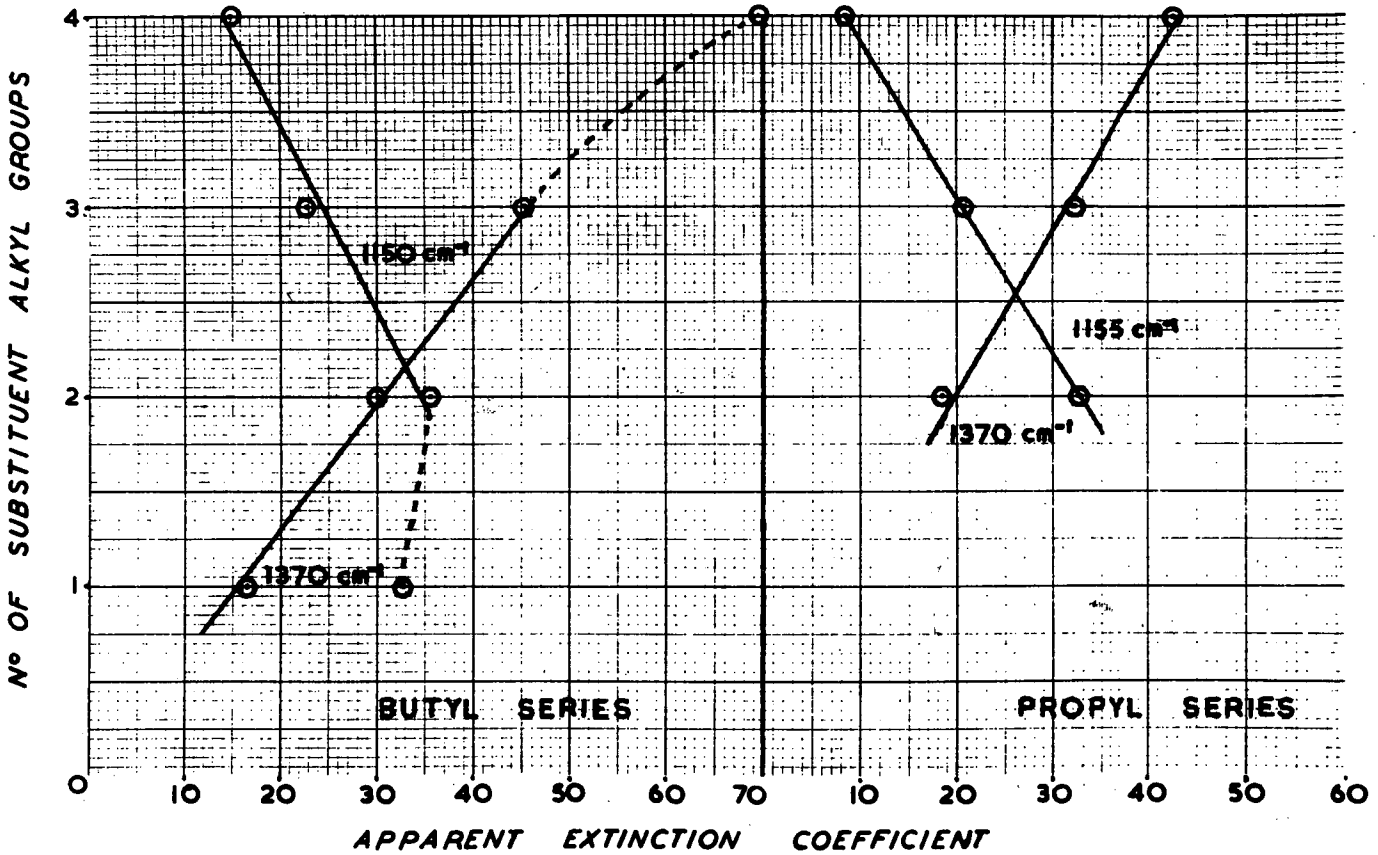

FIG. 1 - EFFECT OF ALKYL GROUPS ON THE EXTINCTION COEFFICIENT OF ALKYLTIN COMPOUNDS

2.6 General

The spectra of the tetraalkyl and tetraaryltin compounds are, as has been noticed by earlier workers, little different from those of mono substituted alkyl or aryl compounds over the range 4000-650 cm^{-1}. If the alkyl or aryl groups are substituted by elements with an atomic weight greater than carbon, it is difficult to detect how many of the alkyl or aryl groups have been replaced.

The two bands near 500 cm^{-1} and 600 cm^{-1} found in the spectra of all the liquid alkyltin compounds examined where the alkyl group is C_3 or more have been identified as belonging to Sn-C stretching frequencies. They arise from two different rotational isomers, trans and gauche, with the higher frequency belonging to the trans isomer.

From this brief survey of the infrared spectra of organotin compounds, it is evident that much more work is necessary in order to interpret the spectra correctly.

3. ACKNOWLEDGEMENT

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4. REFERENCES

1. Ingham, R.K., Rosenberg, S.D. and Gilman, H., 1960, Chem. Reviews, 60, 459.

2. Kettering, C.F. and Sleator, W.W., 1933, Physics, 4, 39.

3. Pai, G., 1935, Proc. Roy. Soc. (London), 149A, 29.

4. Young, C.W., Koehler, J.S. and McKinney, D.S., 1947, J. Am. Chem. Soc., 69, 1410.

5. Siebert, H., 1950, Z. anorg. Chem., 263, 82.

6. Siebert, H., 1952, Z. anorg. Chem., 268, 177.

7. Lippincott, E.R. and Tobin, M.C., 1953, J. Am. Chem. Soc., 75, 4141.

8. Edgell, W.F. and Ward, C.H., 1955, J. Am. Chem. Soc., 77, 6486.

9. Waters, D.N. and Woodward, L.A., 1958, Proc. Royal Soc., A246, 119.

10. Dillard, C.R. and Lawson, J.R., 1960, J. Opt. Soc. Amer., 50, 1271.

11. Bartocha, B., Brinckman, F.E., Kaesz, H.D. and Stone, F.G.A., 1958, Proc. Chem. Soc., 116.

12. Noltes, J.G. and van der Kerk, G.J.M., 1958, - "Functionally Substituted Organotin Compounds." - Tin Research Institute, p. 27.

13. Leavitt, F.C. and Matternas, L.V., 1962, J. Poly. Sci., 62, S.68.

14. Noltes, J.G., Henry, M.C. and Janssen, M.J., 1959, Chem. and Ind., 298.

15. Henry, M.C. and Noltes, J.G., 1960, J. Am. Chem. Soc., 82, 558.

16. Henry, M.C. and Noltes, J.G., 1960, J. Am. Chem. Soc., 82, 555.

17. West, R., Baney, R.H. and Powell, D.L., 1960, J. Am. Chem. Soc., 82, 6269.

18. Margoshes, M. and Fassel, V.A., 1955, Spectrochim. Acta., 7, 14.

19. Harrah, L.A., Ryan, M.T. and Tamborski, C., 1962, Spectrochim. Acta., 18, 21.

20. Poller, R.C., 1962, J. Inorg. Nucl. Chem., 24, 593.

21. Braye, E.H., Hübel, W. and Caplier, I., 1961, J. Am. Chem. Soc., 83, 4406.

22. Friebe, E. and Kelker, H., 1963, Z. analyt. Chem., 192, 267.

23. Kushlefsky, B., Simmons, I. and Ross, A., 1963, Inorg. Chem., 2, 187.

24. Brown, M.P., Okawara, R. and Rochow, E.G., 1960, Spectrochim. Acta., 16, 595.

25. Poller, R.C., 1963, J. Chem. Soc., 706.

26. Okawara, R., Webster, D.E. and Rochow, E.G., 1960, J. Am. Chem. Soc., 82, 3287.

27. Freeman, J.P., 1958, J. Am. Chem. Soc., 80, 5994.

28. Okawara, R. and Sato, H., 1961, J. Inorg. Nucl. Chem., 16, 204.

29. Beattie, I.R. and Gilson, T., 1961, J. Chem. Soc., 2585.

30. Luijten, J.G.A., Janssen, M.J. and van der Kerk, G.J.M., 1962, Rec. trav. chim., 81, 202.

31. van der Kerk, G.J.M., Luijten, J.G.A. and Janssen, M.J., 1962, Chimia, 16, 10.

32. Janssen, M.J., Luijten, J.G.A. and van der Kerk, G.J.M., 1963, Rec. trav. chim., 82, 90.

33. Mathis-Noel, R., Lesbre, M. and Sérée de Roch, I., 1956, C.R. Rebd. Seances Acad. Sci., 243, 257.

34. Behnke, F.W. and Tamborski, C., 1962, A.S.T.I.A. AD.274995, Technical Documentary Report No. ASD-TDR-62-224.

35. Domange, L. and Guy, J., 1958, Ann. pharmac. franc., 16, 161.

36. Kaesz, H.D., Phillips, J.R. and Stone, F.G.A., 1959, Chem. and Ind., 1409.

37. Seyferth, D. and Kahlen, N., 1960, J. Org. Chem., 25, 809.

38. Beattie, I.R., McQuillan, G.P., Rule, L. and Webster, M., 1963, J. Chem. Soc., 1514.

39. Kida, S., Quagliano, J.V., Walmsley, J.A. and Tyree, S.Y., 1963, Spectrochim. Acta., 19, 189.

40. Brown, T.L. and Kubota, M., 1961, J. Am. Chem. Soc., 83, 4175.

41. Sharp, D.W.A. and Sheppard, N., 1957, J. Chem. Soc., 674.

42. Smithson, L.D. and Matta, M.S., - "Infrared Spectra of Some Oils, Greases, Additives and Relative Compounds". - Tech. Doc. Report No. ASD-TDR-62-771, (Wright-Patterson Air Force Base, U.S.A.F.) - A.S.T.I.A. No. AD.287756.

43. Noltes, J.G. and van der Kerk, G.J.M., 1962, Rec. trav. chim., 81, 41.

44. van der Kerk, G.J.M., Luijten, J.G.A. and Noltes, J.G., 1956, Chem. and Ind., 352.

45. Kriegsmann, H. and Pitschschan, S., 1961, Z. anorg. allg. Chemie, 308, 212.

46. Beattie, I.R., McQuillan, G.P. and Hulme, R., 1962, Chem. and Ind., 1429.

47. Okawara, R., Hathaway, B.J. and Webster, D.E., 1963 (Jan.), Proc. Chem. Soc., 13.

48. Hathaway, B.J. and Webster, D.E., 1963 (Jan.), Proc. Chem. Soc., 14.

49. Linnett, J.W., 1945, Trans. Farad. Soc., 41, 223.

50. Alleston, D.L. and Davies, A.G., 1962, J. Chem. Soc., 2050.

51. Montermoso, J.C., Andrews, T.M. and Marinelli, L.P., 1958, J. Poly. Sci., 32, 523.

52. Luijten, J.G.A. and van der Kerk, G.J.M., - "Investigations in the field of Organotin Chemistry", 1955, Tin Research Institute.

53. Brit. Pat. 793,073 (Farbewerke Hoechst Akt.), 1959, Chem. Abs., 53, 22714(i).

54. Hirschfeld, H., 1959, Farbenchemiker, 61, 1, 1960, Chem. Abs., 54, 23363 (h).

55. van der Kerk, G.J.M. and Luijten, J.G.A., 1957, J. appl. Chem., 7, 369.

56. Brit. Pat. 792,309 (Chauny and Cirez), 1958, Chem. Abs., 52, 17805.

57. Pfeiffer, P., Freidmann, B., Lehardt, R., Luftensteiner, H., Prade, R. and Schnurmann, K., 1911, Z. anorg. Chem., 71, 97.

5.1

TABLE I

ASSIGNMENTS OF INFRARED VIBRATIONS INVOLVING TIN-METHYL GROUPS (cm^{-1})

COMPOUND	(Sn-)CH_3 asym. str.	(Sn-)CH_3 rock.	(Sn-)CH_3 sym. def.	(Sn-)CH_3 asym. def.	REFERENCE
Tetramethyltin	ca.530	771 (g), 764 (l)	1190 (l), 1200 (g)	1445 (l), 1447 (g)	4, 7, 8
Trimethyltin formate	552	770 or 790	1195 or 1205	-	26, 28
Trimethyltin acetate	555	775	1194 or 1206	-	28
Trimethyltin chloroacetate	556	765 or 783	1196	-	28
Dimethyltin oxide	550 or 519	714 or 758	1188 or 1206	1410	24
Dimethyltin sulphide (trimer)	517 or 540 or 548	720 or 763 or 782	1193	1409	24
Bis(dimethylchlorotin) oxide	519 or 554	792	1192	1408	24
Methyltin oxide	500	718	1204	1400	24
Dimethyltin diformate	-	770	1202	-	26
Dimethylchlorotin acetate	-	795 or 815	1198 or 1215	-	26
Bis(acetoxydimethyltin) oxide	-	788	1197	-	26
Dimethylchlorotin formate	-	789	1204	-	26
Trimethyltin propionate	-	775	1192 or 1202	-	26
Trimethyltin chloroacetate	-	765 or 783	1196	-	26
Trimethyltin dichloroacetate	-	765	1195 or 1206	-	26
Trimethyltin trichloroacetate	-	772	1195	-	26
Trimethyltin perchlorate	556	-	-	-	47
Trimethyltin tetrafluoroborate	562	-	-	-	48

5.2

T A B L E II

ASSIGNMENTS OF INFRARED VIBRATIONS INVOLVING Sn-X GROUPS

COMPOUND	ASSIGNMENT	FREQUENCY ($cm.^{-1}$)	REFERENCE
Trimethyltin hydride	Sn-H str.	1834	45
Tributyltin hydride	Sn-H str.	1820	33
Dibutyltin dihydride	Sn-H str.	1835	33
Dipropyl-2(-phenylvinyl) tin hydride	Sn-H str.	1824	43
Triphenyltin hydride	Sn-H str.	1825	16
	Sn-H def.	565	34
Trimethyltin chloride	Sn-Cl str.	315 and 336	45 and 46
Trimethyltin chloride pyridinate	Sn-Cl str.	Below 250	46
Bis-(dimethylchlorotin) oxide	Sn-Cl str.	Below 400	24
Phenyltin chlorides	Sn-Cl str.	300-360 depending on compound	19
Triphenyltin chloride	Sn-Cl str.	327	34
Trimethyltin bromide	Sn-Br str.	219	45
Triphenyltin bromide	Sn-Br str.	225	34
Dimethyltin sulphide (trimer)	Sn-S-Sn str.	Below 400	24
Dimethyltin oxide	Sn-O-Sn str.	580	24
Bis-(dimethylchlorotin) oxide	Sn-O-Sn str.	576, 600	24
Methyltin oxide	Sn-O-Sn str.	643	24
Bis-(triphenyltin) oxide	Sn-O-Sn str.	777	20,22,25
Bis-(tri-o-phenoxyphenyltin)oxide	Sn-O-Sn str.	828	25
Triphenyltin hydroxide	Sn-O str. (?)	912, 898	20
Diphenyltin oxide	Sn-O-Sn str.	571, 553	20
Triethyltin hydroxide	Sn-O str. (?)	855	20
Bis-(tripropyltin) oxide	Sn-O-Sn str.	780 - 765, 500	20
Bis-(tributyltin) oxide	Sn-O-Sn str.	787 - 763, 500	20
Tetraphenyltin	Characteristic of tin-phenyl groups	1070	14
Hexaphenylditin	Sn-Sn axial deformation	188 (calc)	19

TABLE III

5.3 BIBLIOGRAPHY OF ORGANOTIN COMPOUNDS

This table lists organotin compounds, by molecular formula, on which some infrared data have been reported. The designation "S" indicates that a spectrum (or part of a spectrum) has been published, while "NS" indicates that no published spectrum is available.

FORMULA	COMPOUND	DESIGNATION	REFERENCE
CH_3SnBr_3	Methyltin tribromide	NS	26
CH_3SnCl_3	Methyltin trichloride	NS	26
CH_3SnI_3	Methyltin triodide	S	26
$CH_3SnO_{3/2}$	Methyltin oxide	S	24, 20
$C_2H_6SnBr_2$	Dimethyltin dibromide	S	26
$C_2H_6SnCl_2$	Dimethyltin dichloride	S	26
$C_2H_6SnI_2$	Dimethyltin diiodide	S	26
C_2H_6SnO	Dimethyltin oxide	S	24, 20
$C_3H_7SnClO_2$	Dimethylchlorotin formate	S	26
$C_3H_9SnBF_4$	Trimethyltin tetrafluoroborate	NS	48
C_3H_9SnBr	Trimethyltin bromide	S	26, 45
C_3H_9SnCl	Trimethyltin chloride	S	46, 45
$C_3H_9SnClO_4$	Trimethyltin perchlorate	NS	47
C_3H_9SnF	Trimethyltin fluoride	S	26, 45
C_3H_9SnI	Trimethyltin iodide	S	26
$C_3H_9SnNO_3$	Trimethyltin nitrate	NS	47
$C_3H_{10}Sn$	Trimethyltin hydride	S	45
$C_4H_6SnCl_4N_2$	Tin tetrachloride bis-(methyl cyanide)	S	40
$C_4H_8SnO_4$	Dimethyltin diformate	S	26, 28

FORMULA	COMPOUND	DESIGNATION	REFERENCE
$C_4 H_9 SnN$	Trimethyltin cyanide	NS	37
$C_4 H_9 SnF_3$	Trimethylperfluoromethyltin	NS	9
$C_4 H_9 SnClO_2$	Dimethylchlorotin acetate	NS	26
$C_4 H_{10} SnI_2$	Diethyltin diiodide	S	35
$C_4 H_{10} SnO_2$	Trimethyltin formate	S	26, 28
$C_4 H_{12} Sn$	Tetramethyltin	S	10, 2 - 8
$C_4 H_{12} Sn_2 Cl_2 O$	Bis-(chlorodimethyltin) oxide	S	24
$C_5 H_9 SnCl_3 O_2$	Trimethyltin trichloroacetate	NS	26
$C_5 H_9 SnF_5$	Trimethylperfluoroethyltin	NS	9
$C_5 H_{10} SnCl_2 O_2$	Trimethyltin dichloroacetate	NS	26
$C_5 H_{11} SnCl_2$	Trimethyltin chloroacetate	S	26, 28
$C_5 H_{11} SnN_3$	N-trimethyltin triazole	NS	30, 31
$C_5 H_{11} SnO_2$	Trimethyltin acetate	S	26,28,29,32
$C_5 H_{14} Sn$	Trimethylethyltin	S	10
$C_6 H_5 SnCl_3$	Phenyltin trichloride	NS	20
$C_6 H_5 SnI_3$	Phenyltin triodide	NS	20
$C_6 H_{12} SnN_2$	N-trimethyltin imidazole	NS	30, 31
$C_6 H_{12} SnO_4$	Dimethyltin diacetate	NS	29
$C_6 H_{14} SnCl_2$	Dipropyltin dichloride	S	33
$C_6 H_{14} SnO_2$	Trimethyltin propionate	NS	26
$C_6 H_{15} SnI$	Triethyltin iodide	S	35
$C_6 H_{16} Sn$	Dipropyltin dihydride	S	33
$C_6 H_{16} Sn$	Dimethyldiethyltin	S	10
$C_6 H_{16} SnO$	Triethyltin hydroxide	S	35, 20
$C_6 H_{18} Sn_3 S_3$	Dimethyltin sulphide (trimer)	S	24

FORMULA	COMPOUND	DESIGNATION	REFERENCE
$C_7H_{13}SnN$	N-trimethyltin pyrrole	NS	30, 31
$C_7H_{18}Sn$	Methyltriethyltin	S	10
$C_8H_{12}Sn$	Tetravinyltin	NS	11
$C_8H_{14}SnClN$	Trimethyltin chloride pyridinate	NS	46
$C_8H_{18}SnCl_2$	Dibutyltin dichloride	S	33
$C_8H_{18}SnO_2$	Triethyltin acetate	NS	32
$C_8H_{18}Sn_2O_5$	Bis-(acetoxydimethyltin) oxide	S	26
$C_8H_{20}Sn$	Dibutyltin dihydride	S	33
$C_8H_{20}Sn$	Tetraethyltin	S	16, 10
$C_9H_{21}SnCl$	Tripropyltin chloride	S	33
$C_9H_{22}Sn$	Tripropyltin hydride	S	33
$C_{10}H_8SnCl_4N_2$	Tin tetrachloride, 2,2'-bipyridyl	NS	40
$C_{10}H_{10}SnCl_4N_2$	Tin tetrachloride dipyridinate	NS	40
$C_{10}H_{10}SnBr_4N_2O_2$	Tin tetrabromide di-(pyridine N-oxide)	NS	39
$C_{12}H_8SnCl_4N_2$	Tin tetrachloride 1,10-phenanthroline	NS	40
$C_{12}H_{10}SnCl_2$	Diphenyltin dichloride	S	19, 20
$C_{12}H_{10}SnI_2$	Diphenyltin diiodide	NS	20
$C_{12}H_{10}SnO$	Diphenyltin oxide	S(22)	20, 22
$C_{12}H_{10}SnS$	Diphenyltin sulphide	NS	20
$C_{12}H_{20}Sn$	Phenyltriethyltin	S	16
$C_{12}H_{24}SnO_4$	Dibutyltin diacetate	S	14
$C_{12}H_{27}SnCl$	Tributyltin chloride	S	33
$C_{12}H_{28}Sn$	Tributyltin hydride	S	33
$C_{14}H_{22}Sn$	Dipropyl-(2-phenylvinyl)tin hydride	NS	43
$C_{14}H_{30}SnO_2$	Tributyltin acetate	NS	32

FORMULA	COMPOUND	DESIGNATION	REFERENCE
$C_{15}H_{32}SnO_2$	Trimethyltin laurate	S	32
$C_{16}H_{16}Sn$	Diphenyldivinyltin	S	16
$C_{16}H_{30}SnO_4$	Stannous octanoate	S	42
$C_{18}H_{15}SnBr$	Triphenyltin bromide	S	34, 20
$C_{18}H_{15}SnCl$	Triphenyltin chloride	S	19,20,22,34
$C_{18}H_{15}SnI$	Triphenyltin iodide	NS	20
$C_{18}H_{15}SnF$	Triphenyltin fluoride	NS	20
$C_{18}H_{15}SnDO$	Triphenyltin deuteroxide	S	22
$C_{18}H_{16}Sn$	Triphenyltin hydride	S	16, 34
$C_{18}H_{16}SnO$	Triphenyltin hydroxide	S(22)	20,17,22,23
$C_{18}H_{20}Sn$	Diphenyldiallyltin	S	16
$C_{18}H_{42}Sn_2O$	Bis-(tripropyltin) oxide	NS	20
$C_{19}H_{15}SnCl_5$	Triphenylmethyl pentachlorostannate	S	41
$C_{20}H_{15}SnF_5$	Triphenylperfluoroethyltin	NS	9
$C_{20}H_{17}SnN$	Triphenylcyanomethyltin	NS	48
$C_{20}H_{18}Sn$	Triphenylvinyltin	S	16
$C_{20}H_{18}SnO_2$	Triphenyltin acetate	NS	20
$C_{20}H_{20}Sn$	Triphenylethyltin	NS	12
$C_{20}H_{38}SnO_4$	Stannous caprate	S	42
$C_{20}H_{42}SnO_2$	Trihexyltin acetate	NS	32
$C_{20}H_{42}SnO_2$	Tributyltin octanoate	NS	50
$C_{21}H_{19}SnN$	Triphenylcyanoethyltin	NS	44
$C_{21}H_{20}Sn$	Triphenylallyltin	S	16
$C_{22}H_{26}SnN_2S_4$	Dibutyltin bis-(2-mercaptobenzthiazole)	S	42
$C_{24}H_{19}SnNO_3$	Triphenyltin p-nitrophenoxide	NS	20

FORMULA	COMPOUND	DESIGNATION	REFERENCE
$C_{24}H_{20}Sn$	Tetraphenyltin	S	14,19,20,22
$C_{24}H_{18}SnO_3$	Di(o-phenoxyphenyl)tin oxide	NS	25
$C_{24}H_{20}SnS$	Triphenyltin thiophenoxide	NS	20
$C_{24}H_{54}Sn_2O$	Bis-(tributyltin) oxide	NS	20
$C_{25}H_{20}SnO_2$	Triphenyltin benzoate	NS	20
$C_{25}H_{22}SnO_3S$	Triphenyltin p-toluene sulphonate	NS	20
$C_{26}H_{54}SnO_2$	Trioctyltin acetate	NS	30, 32
$C_{36}H_{30}SnGe$	Triphenyltin triphenylgermane	S	19
$C_{36}H_{30}SnSi$	Triphenyltin triphenylsilane	S	19
$C_{36}H_{30}Sn_2$	Hexaphenylditin	S	19, 16
$C_{36}H_{30}Sn_2O$	Bis-(triphenyltin) oxide	S(22)	20, 22, 23
$C_{36}H_{30}Sn_2S$	Bis-(triphenyltin) sulphide	NS	20
$C_{38}H_{34}Sn_2$	Bis-(triphenyltin) ethane	S	12, 15
$C_{38}H_{34}SnSi$	1-Triphenylstannyl-2-triphenylsilyl ethane	S	15
$C_{38}H_{34}SnGe$	1-Triphenylstannyl-2-triphenyl germyl ethane	S	15
$C_{40}H_{30}Sn$*	Hexaphenylstannole	S	21
$C_{40}H_{34}Sn_2$	1,3-Butadienylenebis-(triphenyltin)	NS	13
$C_{46}H_{38}Sn_2$	p-Phenylenedivinylenebis-(triphenyltin)	NS	13
$C_{48}H_{38}O_7Sn_2$	Bis-(hydroxy di-o-phenoxyphenyltin) oxide	NS	25
$C_{52}H_{48}Sn_2Si$	Diphenyl-bis-(2-triphenylstannyl)-ethyl-silane	NS	25
$C_{52}H_{48}Sn_2Ge$	Diphenyl-bis-(2-triphenylstannyl)-ethyl-germane	NS	25
$C_{56}H_{40}Sn$*	Octaphenyl-5-stannaspiro(4,4)nona-1,3,6,8, -tetraene	S	21
$C_{72}H_{54}O_7Sn_2$	Bis-(tri-o-phenoxyphenyltin) oxide	NS	25

* For spectra see Sadtler Midget Edition Nos. 20,957 and 20,958.

6. SPECTRA

The spectra in this section have been classified by functional group. Compounds were either obtained from commercial sources or prepared at D.S.L. Commercial compounds were examined without further purification.

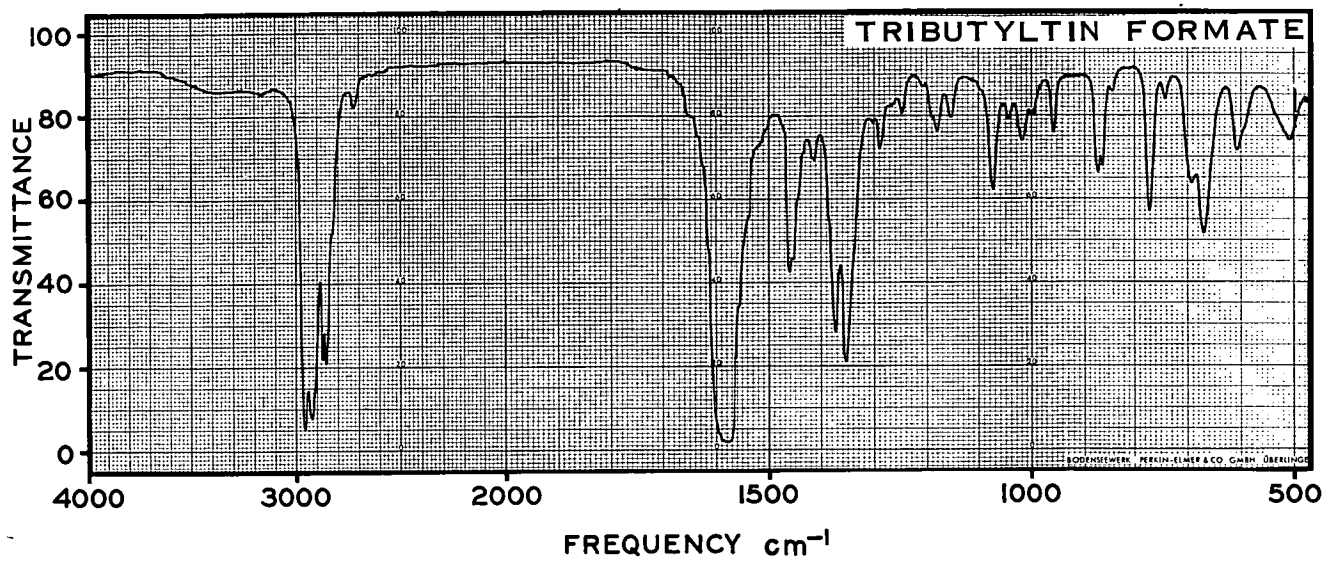
Where previously reported compounds were prepared at D.S.L., the reference to the method of preparation is given. Where no reference is given, this indicates that the compounds have not previously been reported.

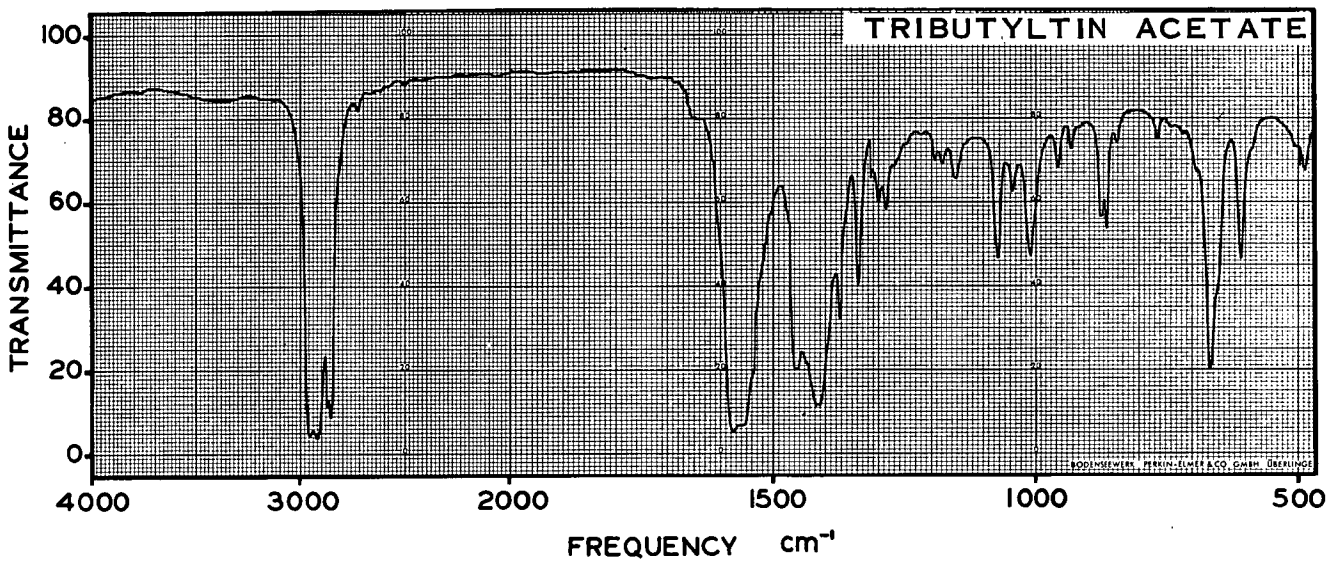
The following abbreviations have been used in Sections 6.1 - 6.13.

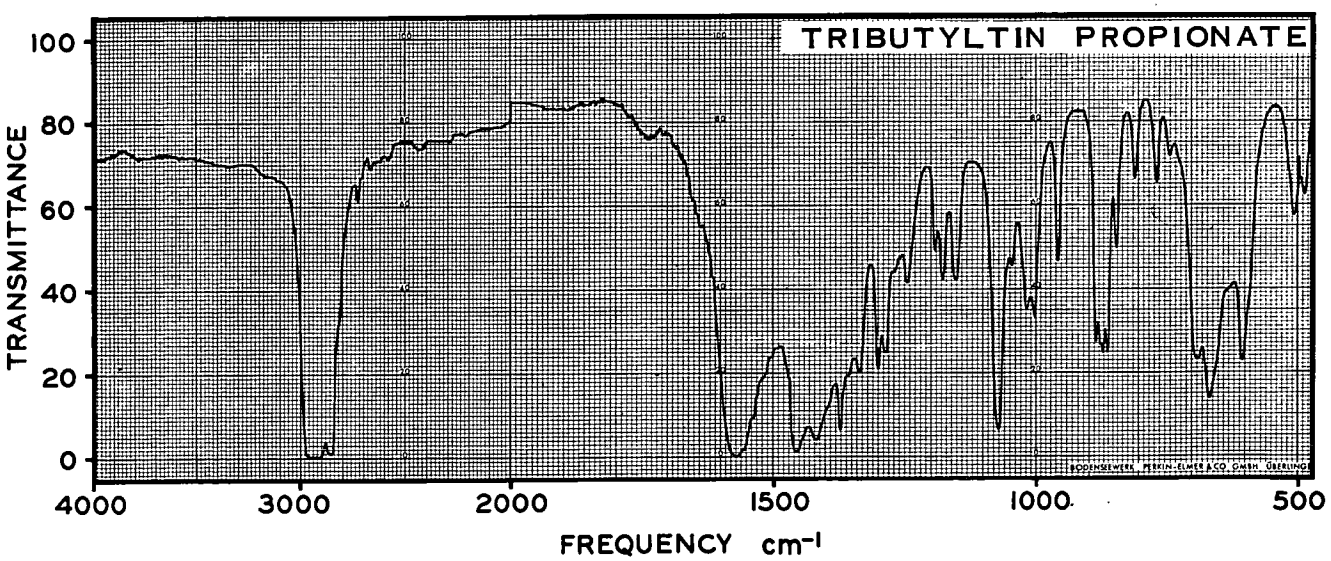
D.S.L.	-	Defence Standards Laboratories, Melbourne, Australia.
N.P.	-	Nuodex Products Company, New Jersey, U.S.A.
P.C.L.	-	Pure Chemicals Limited, Liverpool, England.
P.C.D.	-	Plains Chemical Development Co., New Jersey, U.S.A.
A.S.C.	-	Advance Solvents and Chemical Co., New Jersey, U.S.A.
		or
		Deutsche Advance Production, G.m.B.H., Germany.
A.W.	-	Albright and Wilson, Ltd., Oldbury, England.
M.T.	-	Metal and Thermit Corporation, New Jersey, U.S.A.
D.	-	Potassium bromide disc
X.C.	-	Crystalline capillary
C.F.	-	Capillary film
N.M.	-	Nujol mull

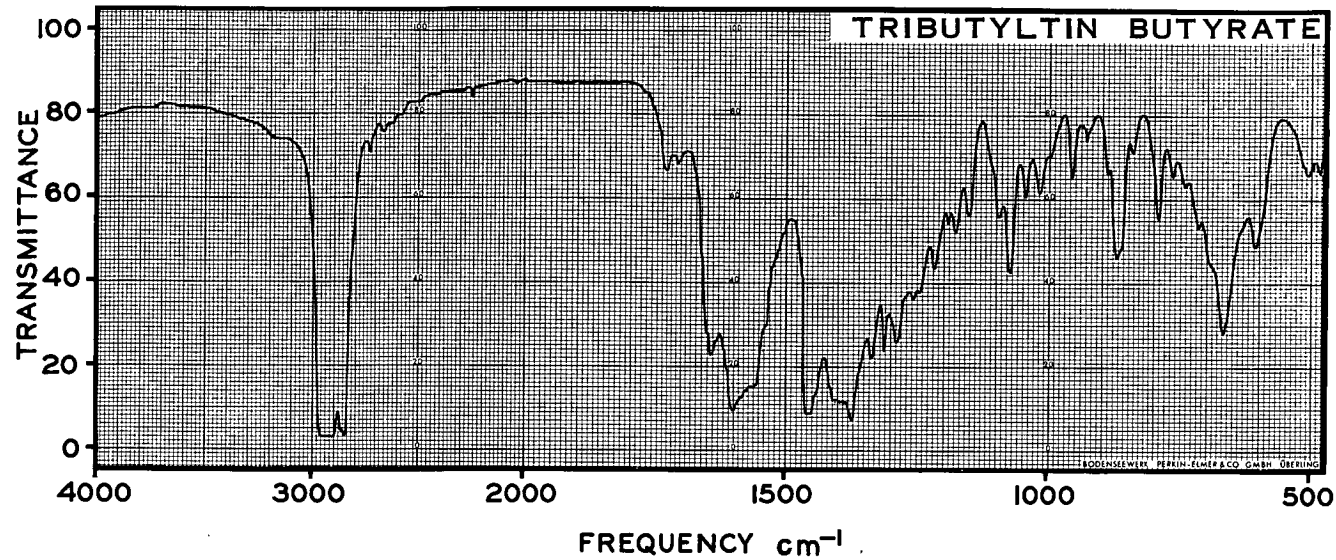
6.1 Organotin Saturated Aliphatic Carboxylates

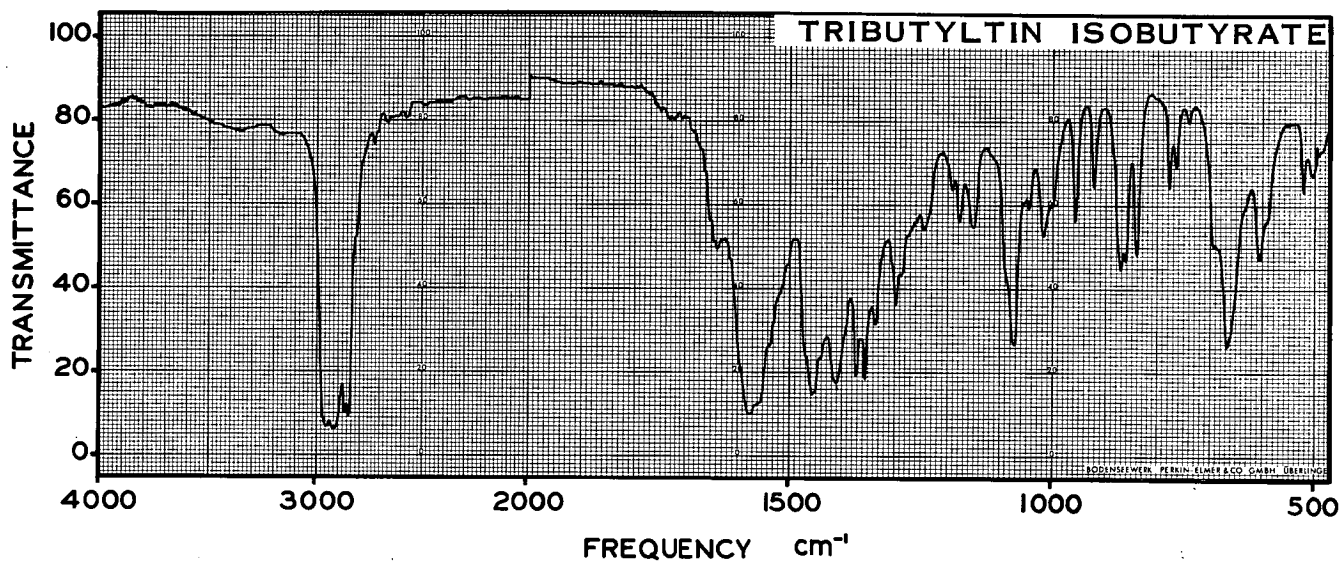
SPECTRUM NO.	COMPOUND	SOURCE AND REFERENCE	SAMPLE FORM
1	Tributyltin formate	D.S.L.	C.F.
2	Tributyltin acetate	A.S.C.	N.M.
3	Tributyltin propionate	D.S.L.	X.C.
4	Tributyltin butyrate	D.S.L.	X.C.
5	Tributyltin isobutyrate	D.S.L.	X.C.
6	Tributyltin valerate	D.S.L.	X.C.
7	Tributyltin isovalerate	D.S.L.	X.C.
8	Tributyltin caproate	D.S.L., 50	X.C.
9	Tributyltin isocaproate	D.S.L.	X.C.
10	Tributyltin heptylate	D.S.L.	X.C.
11	Tributyltin caprylate	D.S.L.	C.F.
12	Tributyltin pelargonate	D.S.L.	X.C.
13	Tributyltin caprate	D.S.L.	C.F.
14	Tributyltin undecylate	D.S.L.	C.F.
15	Tributyltin laurate	P.C.D.	C.F.
16	Tributyltin tridecylate	D.S.L.	C.F.
17	Tributyltin myristate	D.S.L.	C.F.
18	Tributyltin pentadecylate	D.S.L.	C.F.
19	Tributyltin palmitate	D.S.L.	C.F.
20	Tributyltin margarate	D.S.L.	C.F.
21	Tributyltin stearate	D.S.L.	C.F.

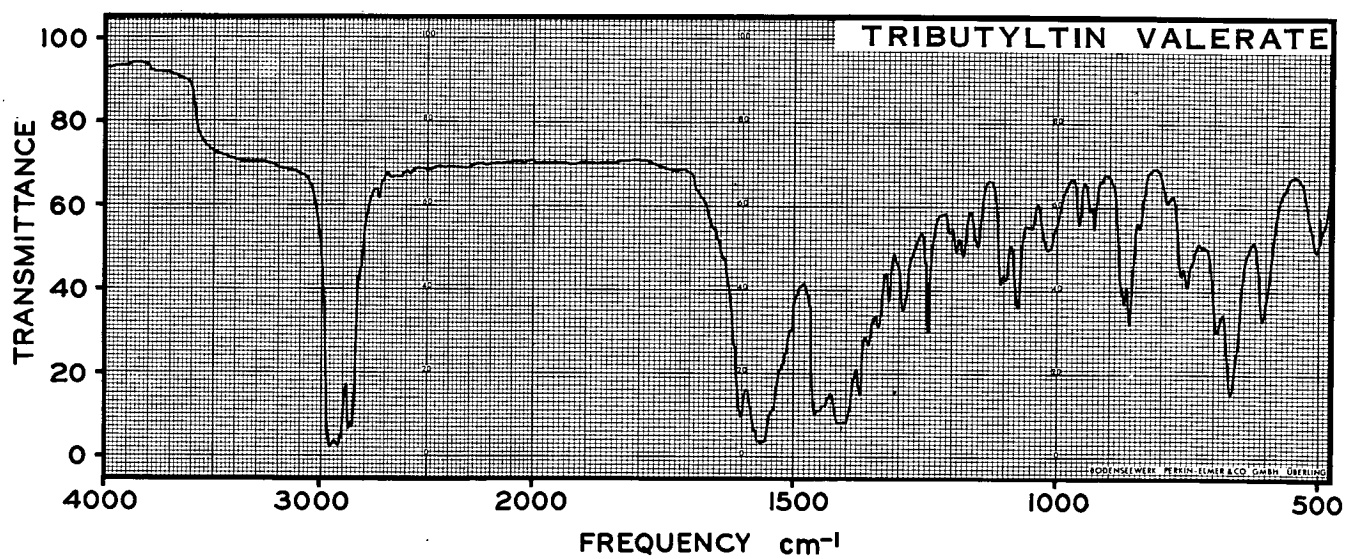

TRIBUTYLTIN FORMATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹

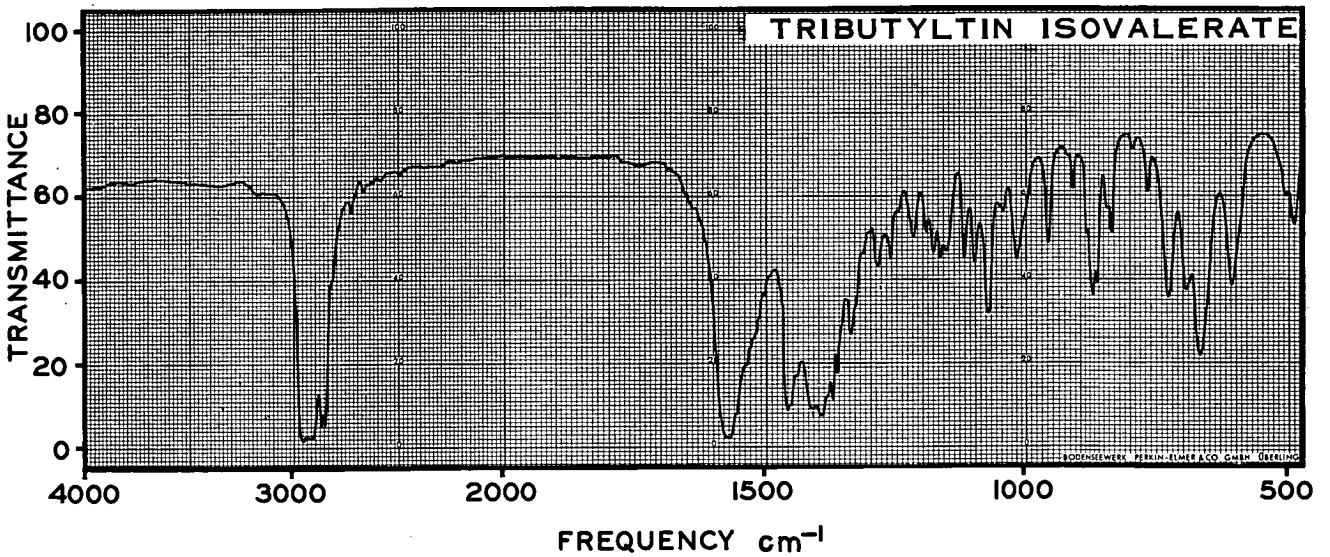

TRIBUTYLTIN ACETATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹

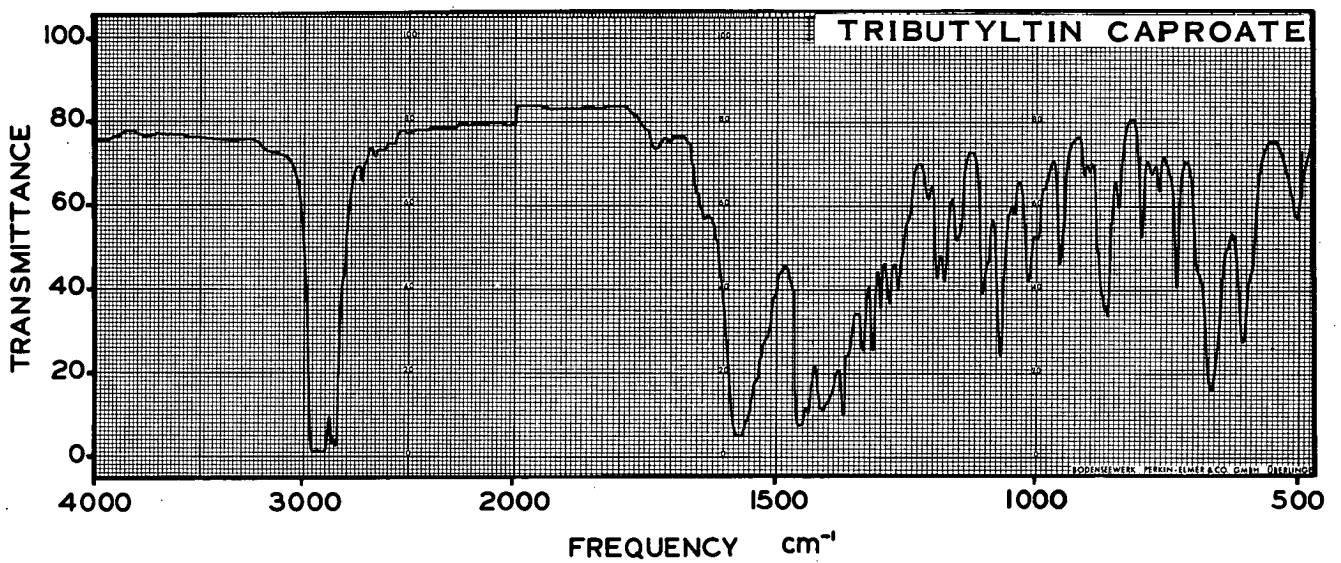

TRIBUTYLTIN PROPIONATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹

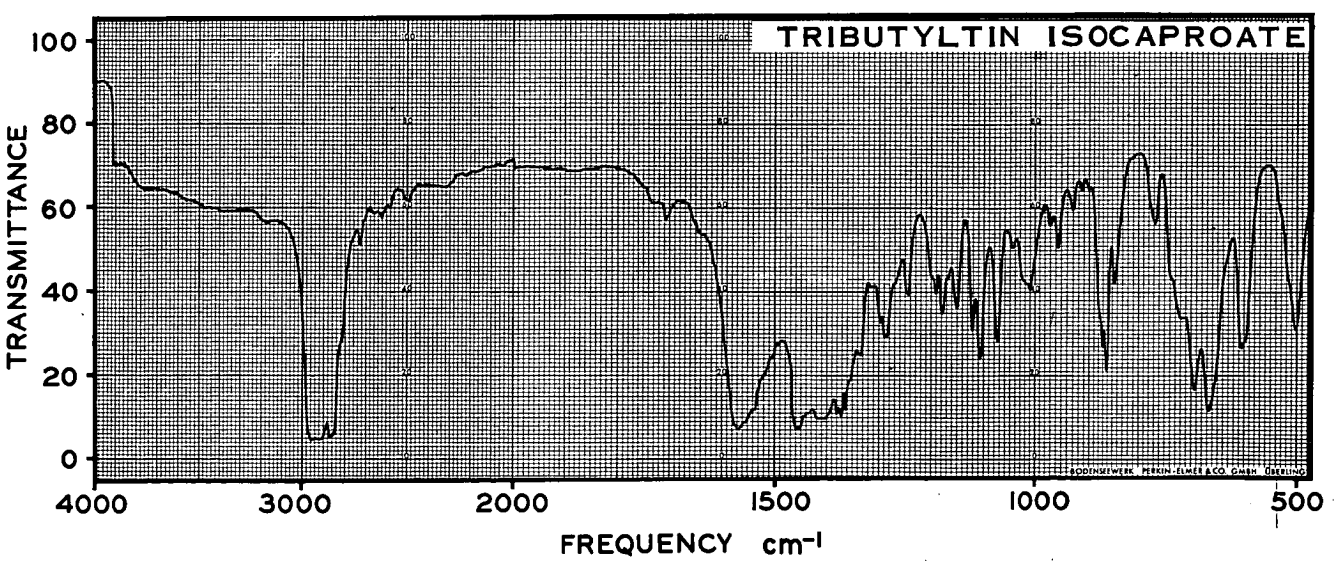

TRIBUTYLTIN BUTYRATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹
BODENSEEWERK PERKIN-ELMER & CO GMBH ÜBERLINGEN

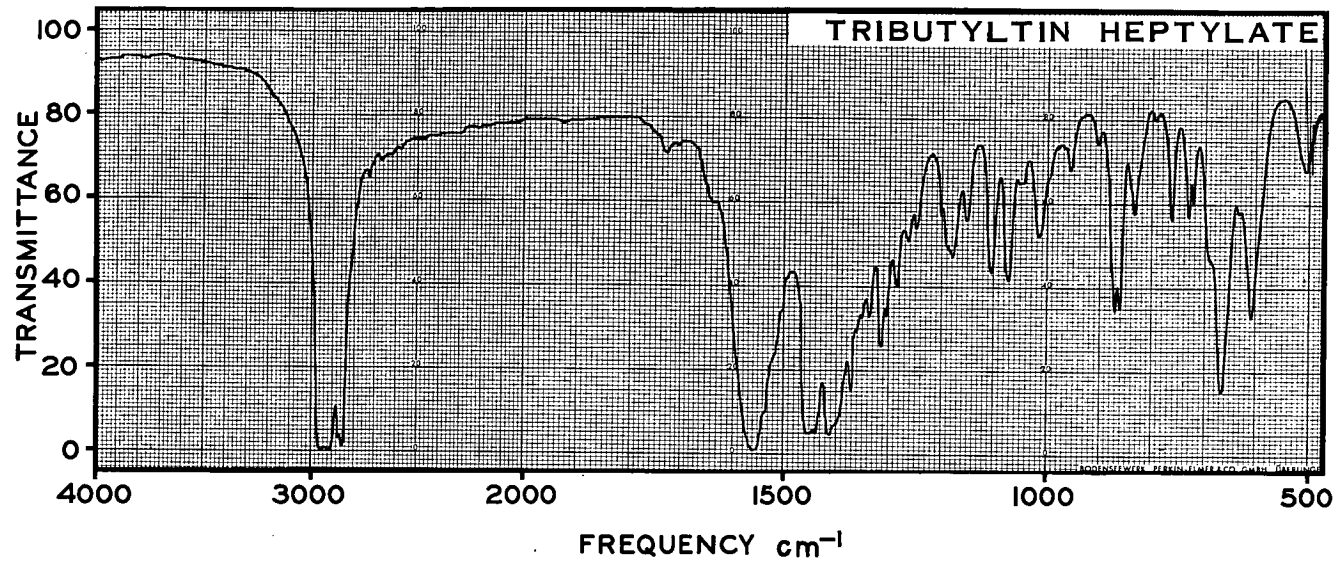

TRIBUTYLTIN ISOBUTYRATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹
BODENSEEWERK PERKIN-ELMER & CO GMBH ÜBERLINGEN

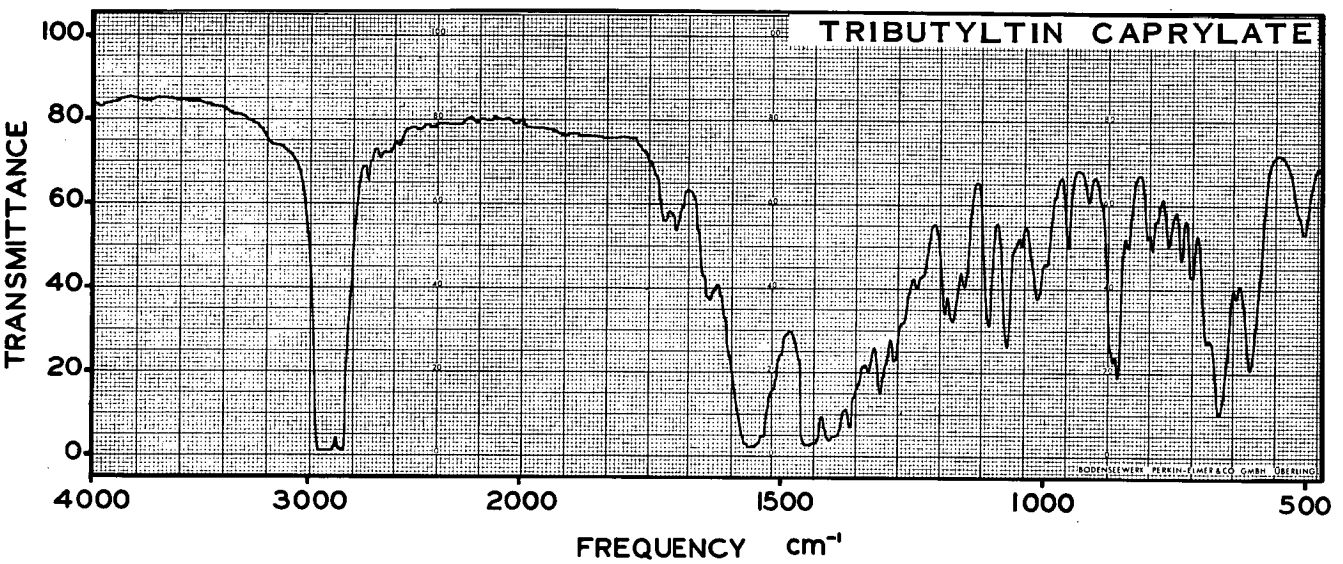

TRIBUTYLTIN VALERATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹
BODENSEEWERK PERKIN-ELMER & CO GMBH ÜBERLINGEN

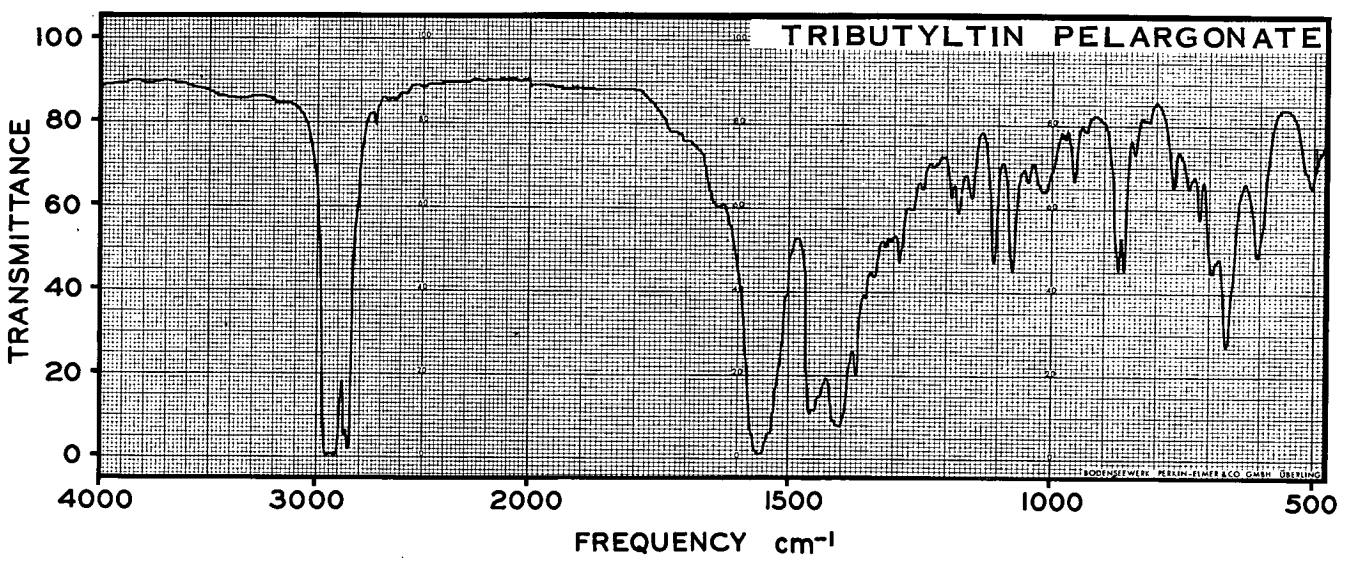

TRIBUTYLTIN ISOVALERATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹


TRIBUTYLTIN CAPROATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹


TRIBUTYLTIN ISOCAPROATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹

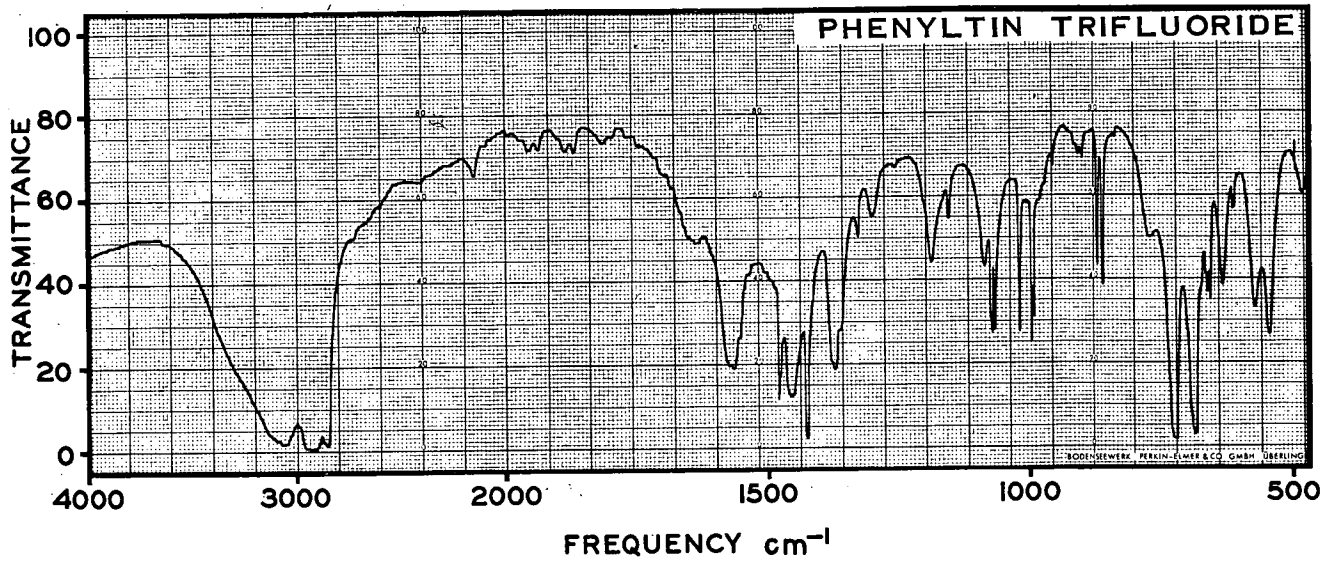

TRIBUTYLTIN HEPTYLATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹

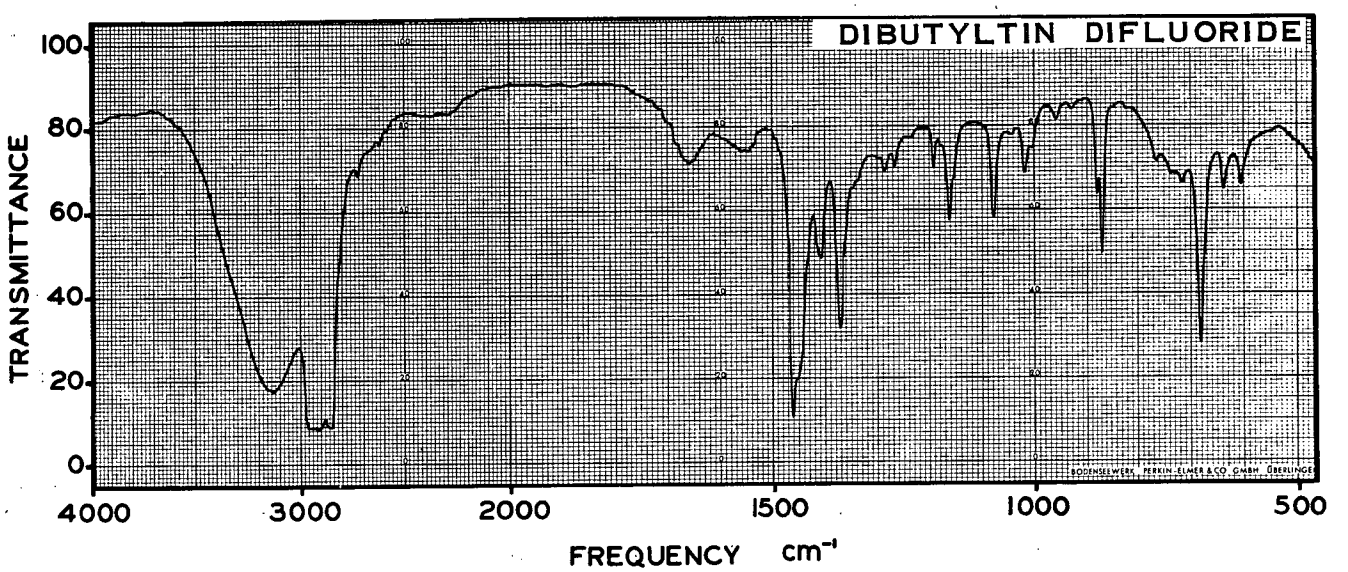

TRIBUTYLTIN CAPRYLATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹

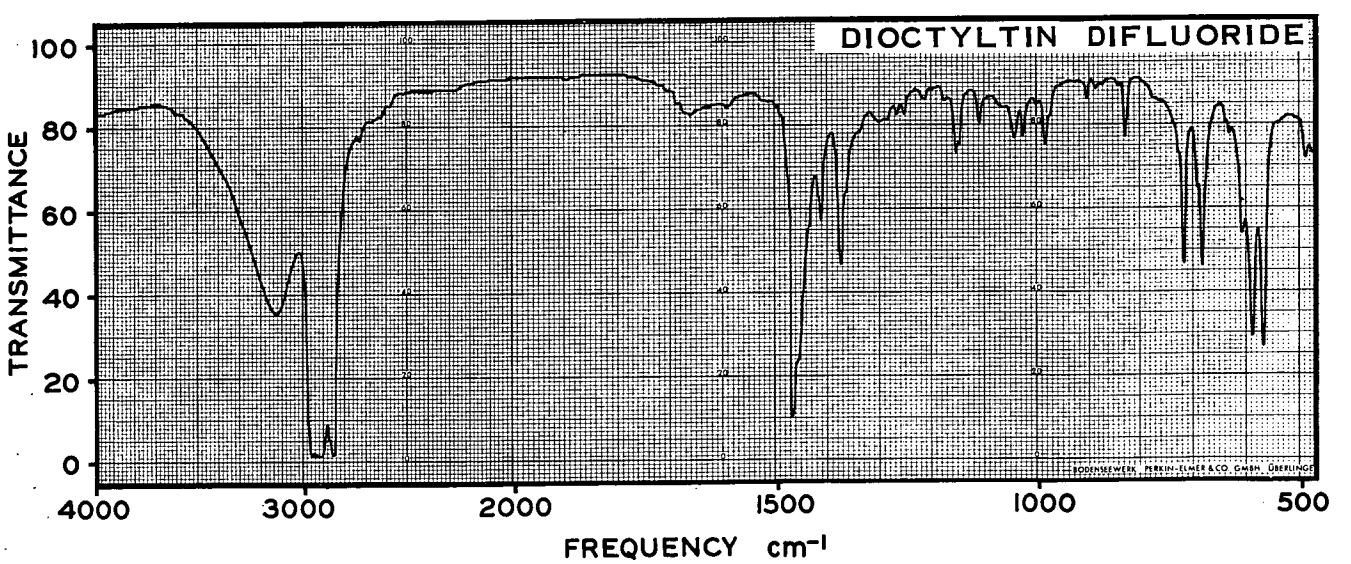

TRIBUTYLTIN PELARGONATE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹

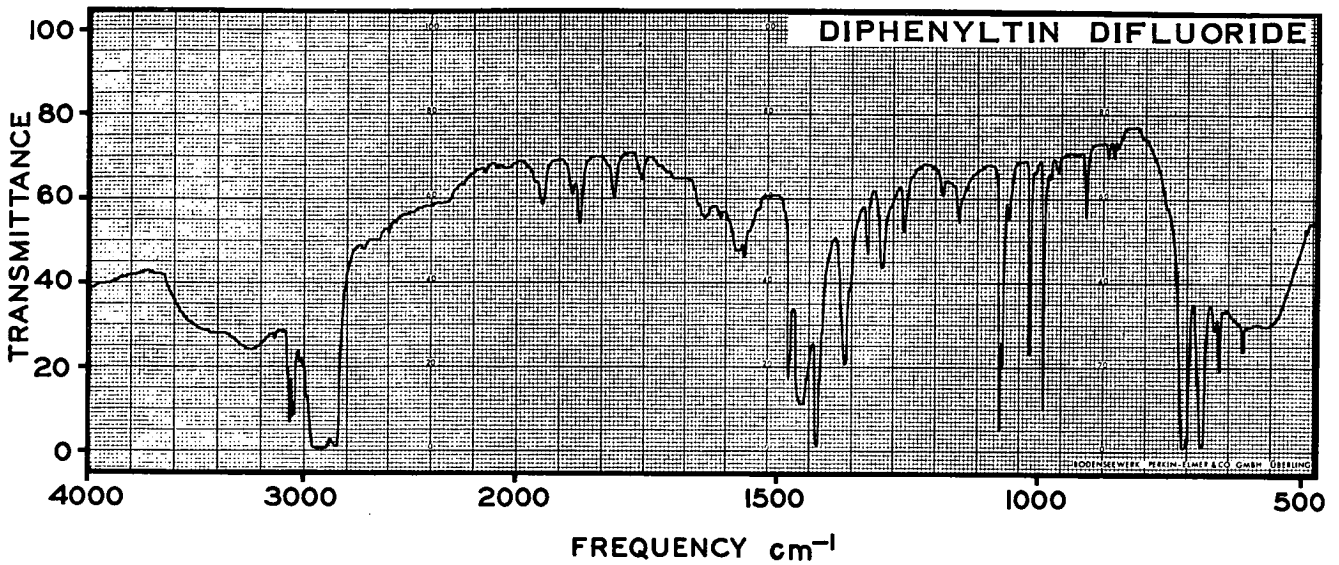
6.10 Organotin Fluoride

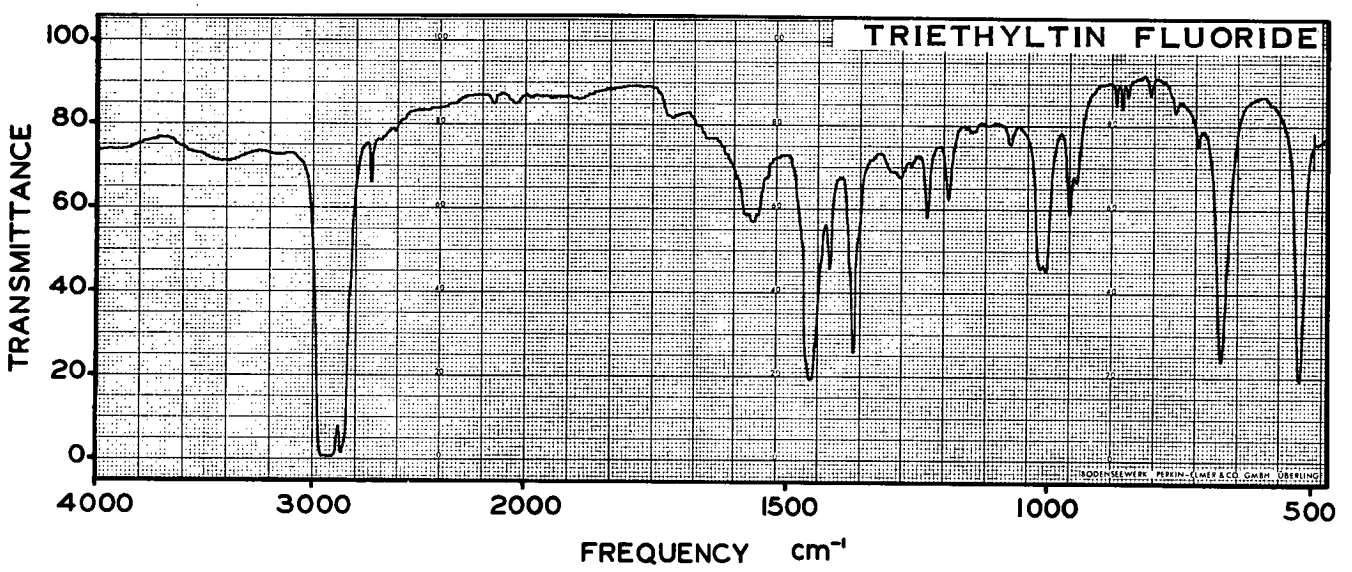
SPECTRUM NO.	COMPOUND	SOURCE AND REFERENCE	SAMPLE FORM
1	Phenyltin trifluoride	D.S.L.	N.M.
2	Dibutyltin difluoride	D.S.L., 50	N.M.
3	Dioctyltin difluoride	D.S.L.	N.M.
4	Diphenyltin difluoride	D.S.L.	N.M.
5	Triethyltin fluoride	D.S.L., 1	N.M.
6	Tributyltin fluoride	D.S.L.	N.M.
7	Triphenyltin fluoride	D.S.L., 1	N.M.

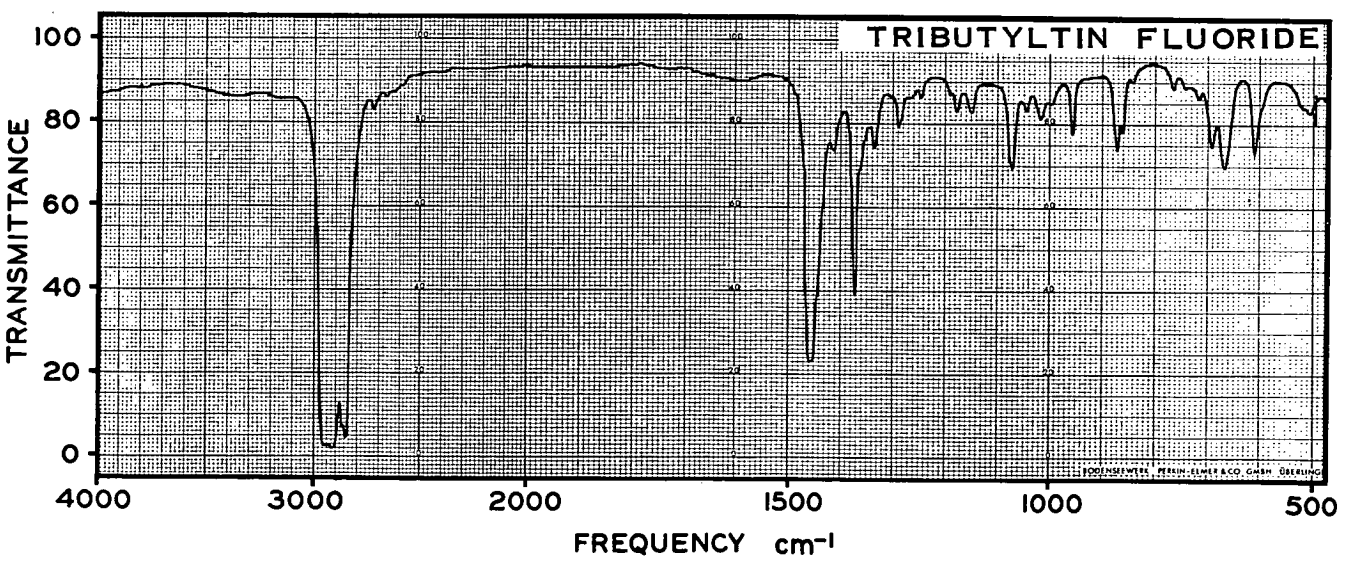

PHENYLTIN TRIFLUORIDE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹


DIBUTYLTIN DIFLUORIDE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹


DIOCTYLTIN DIFLUORIDE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹


DIPHENYLTIN DIFLUORIDE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹


TRIETHYLTIN FLUORIDE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹


TRIBUTYLTIN FLUORIDE
TRANSMITTANCE
100
80
60
40
20
0
4000
3000
2000
1500
1000
500
FREQUENCY cm⁻¹

APPENDIX 10 INFRARED STUDIES ON ORGANOTIN COMPOUNDS

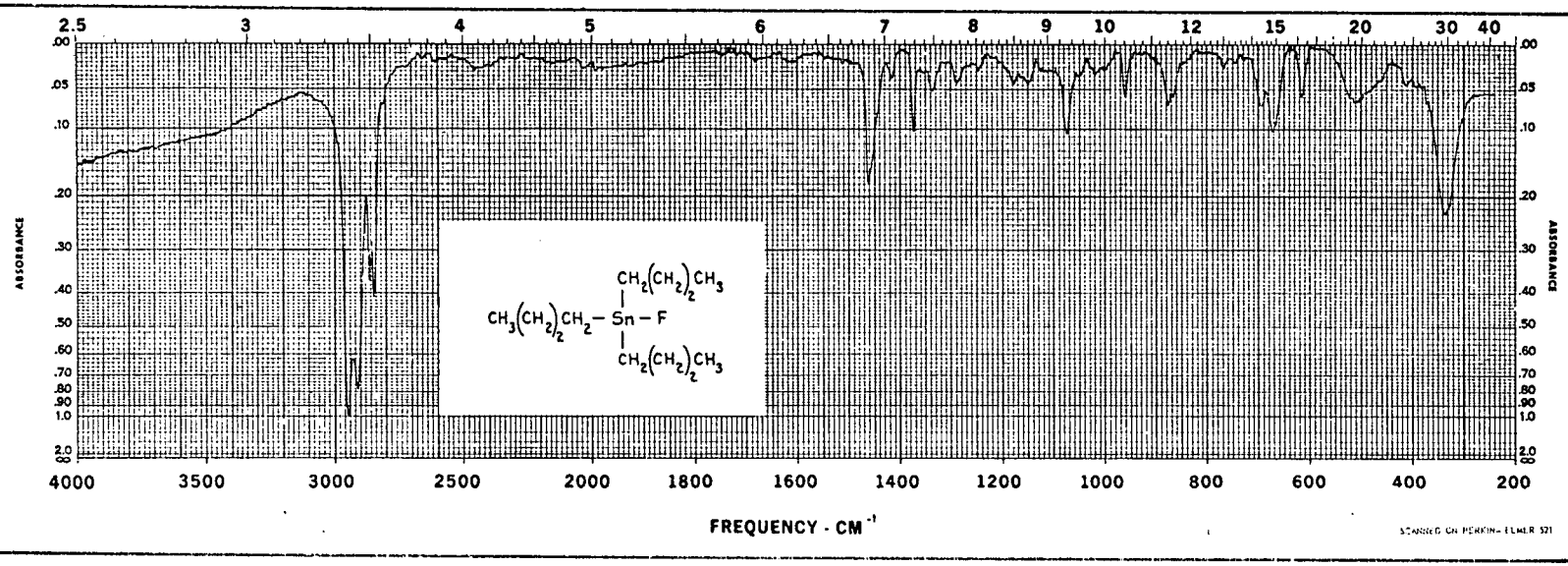
10b Sadtler Infrared Spectra of Organotin Compounds.

Four spectra are reproduced as examples of the fifty-one spectra issued by Sadtler from MRL-supplied compounds, namely:

N229K	Fluorotributyltin	
N230K	Fluorotriphenyltin	10.35
N231K	(Isothiocyanato)tributyltin	
N232K	Succinimidotributyltin	10.36

Note: The Sadtler spectra may be compared with the MRL spectra issued in Report 266 (78), Appendix 10a. For example tributyltin fluoride, N229K above (10.35) appears in Appendix 10a as Spectrum No. 6, Section 6.10, Organotin Fluorides.

FLUOROTRIBUTYLTIN



$C_{12}H_{27}FSn$
M.W. 309.04

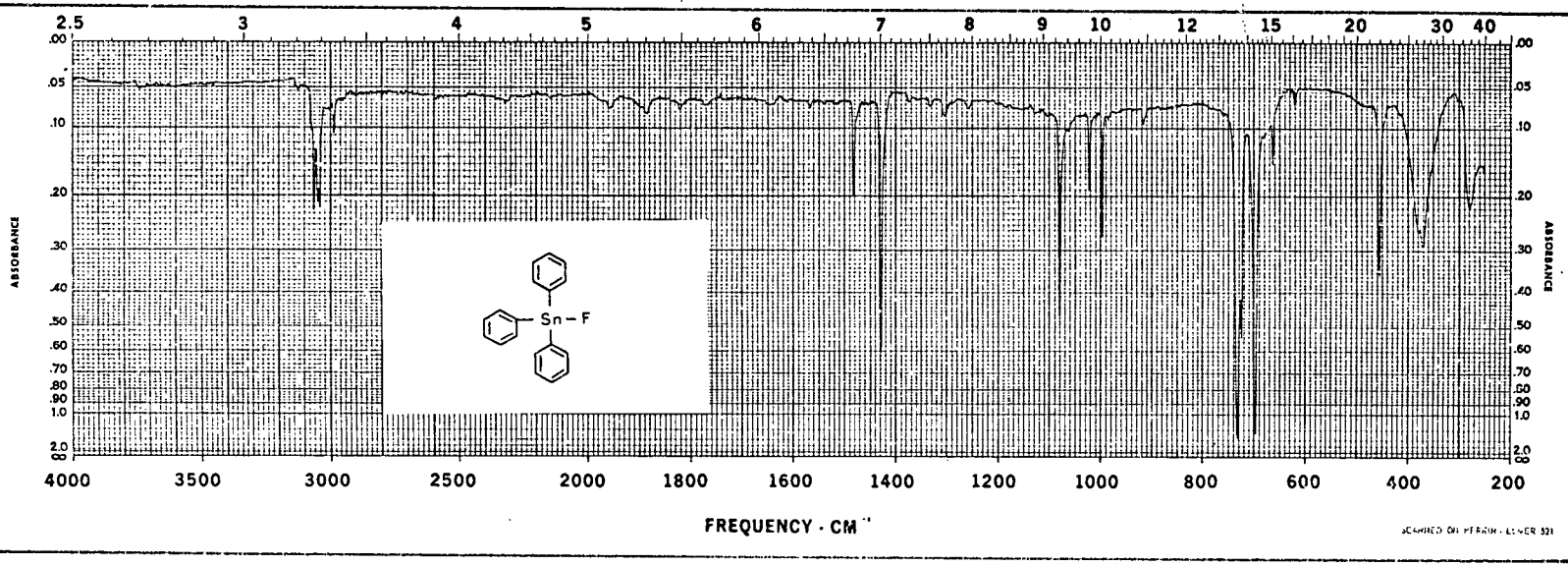
Ref.:
CA 60, 11503 (1964)

KBr Wafer

Source: Defence Standards Laboratories, Victoria, Australia

N 229 K

FLUOROTRIPHENYLTIN



$C_{18}H_{15}FSn$
M.W. 369.01
M.P. 357°C (lit.)

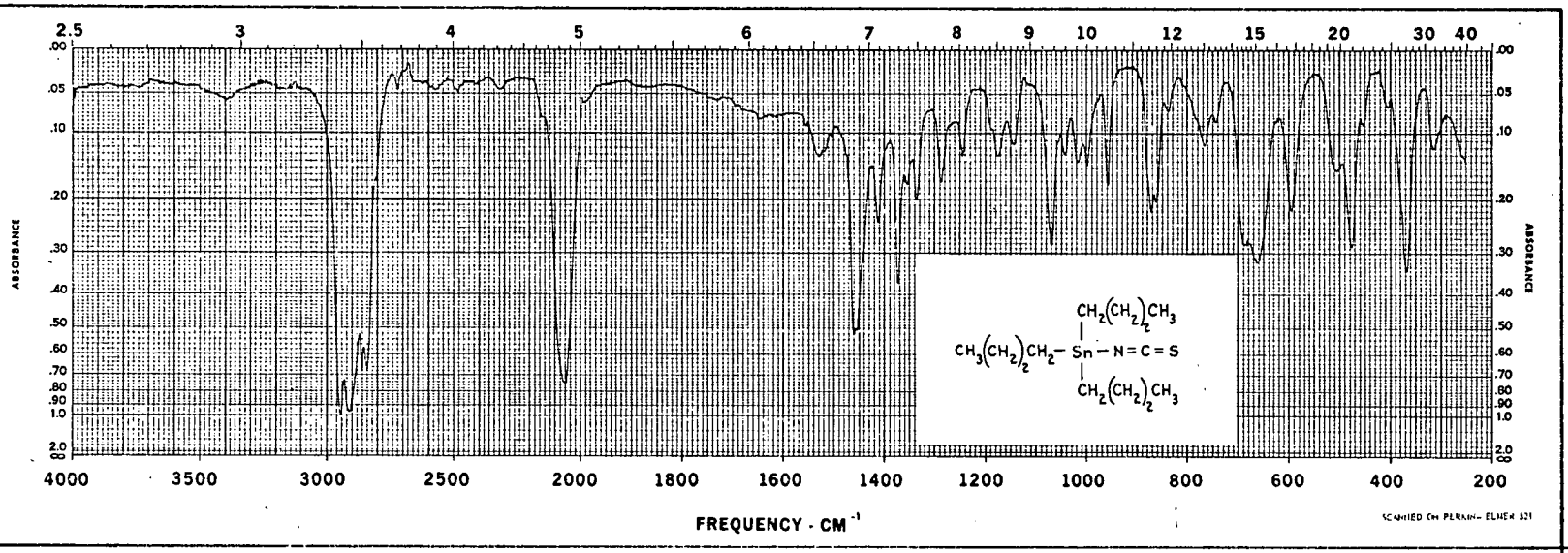
Ref.:
CA 60, 11503 (1964)

KBr Wafer

Source: Defence Standards Laboratories, Victoria, Australia

N 230 K

(ISOTHIOCYANATO)TRIBUTYLTIN



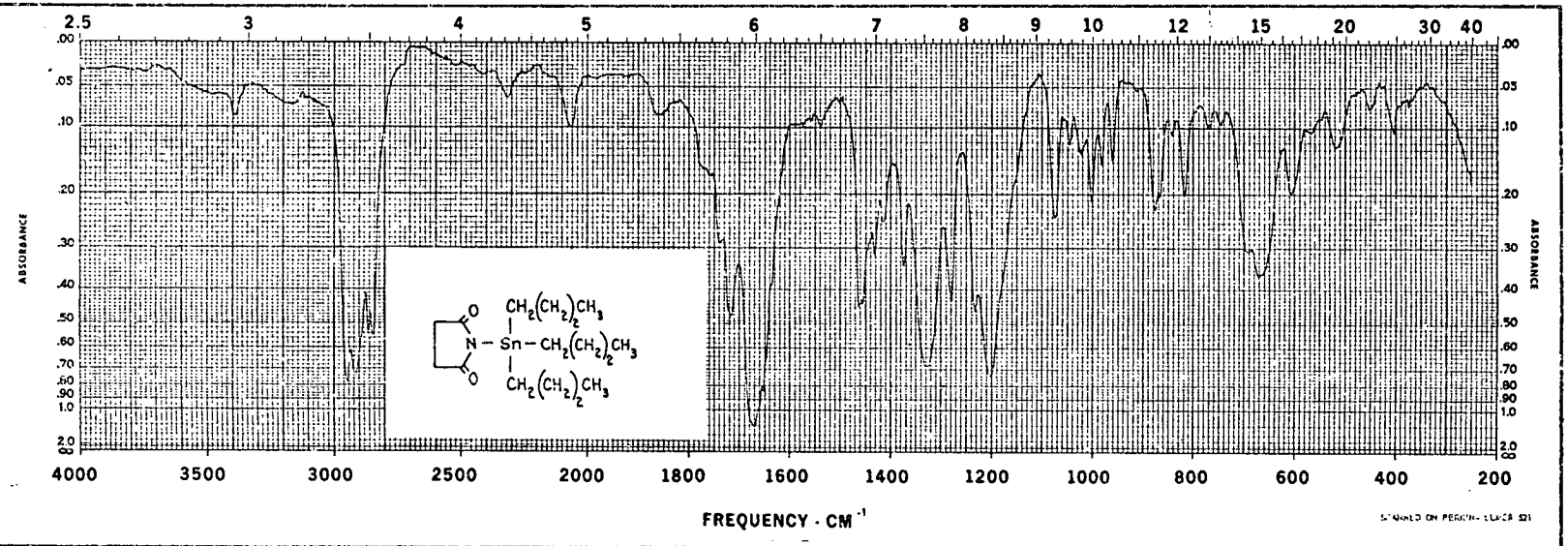
$C_{13}H_{27}NSSn$
M.W. 348.12
B.P. 146°C/0.2mm
n_D^{20} 1.5432 (lit.)
Ref.:
CA 60, 11503 (1964)

Capillary Cell:
Neat

Source: Defence Standards Laboratories, Victoria, Australia

N 231 K

SUCCINIMIDOTRIBUTYLTIN



$C_{16}H_{31}NO_2Sn$
M.W. 388.12
M.P. 21°C
B.P. 144°C/0.2mm
n_D^{20} 1.5086 (lit.)
Ref.:
CA 60, 11503 (1964)

Capillary Cell:
Neat

Source: Defence Standards Laboratories, Victoria, Australia

N 232 K

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ORGANOTIN CARBOXYLATES

By R. A. Cummins and P. Dunn

APPENDIX 10c

10.37 - 10.44

ORGANOTIN CARBOXYLATES*

By R. A. CUMMINS† and P. DUNN†

[*Manuscript received August* 19, 1963]

Summary

The homologous series of tributyltin carboxylates ranging from the formate to the stearate and three substituted tributyltin acetates have been prepared. Examination of the infrared spectra of the compounds supports the recent view that organotin esters are covalent and chelated in character rather than ionic compounds.

INTRODUCTION

Freeman,[1] Okawara, Webster, and Rochow,[2] and Okawara and Sato[3] from a study of methyltin esters inferred that the carboxylate group was ionic, and that the dimethyltin and trimethyltin groups existed as cations. However, Beattie and Gilson[4] and van der Kerk and co-workers[5,6] have proposed that the organotin esters exist as chelated covalent compounds involving a five-coordinated tin atom. Similar suggestions have also been made by Beattie, McQuillan, and Hulme,[7] Okawara, Hathaway, and Webster[8] and Hathaway and Webster[9] concerning the presence of five-coordinate tin in other organotin compounds. Poller[10] on the other hand studied the C=O stretching frequencies of organotin esters, but was unable to distinguish between an ionic and a covalent structure.

Recently, after completion of our experimental work, Janssen, Luijten, and van der Kerk[11] reported infrared investigations on the structure of trialkyltin acylates. Although different organotin compounds were studied by these workers, their results and ours are in good agreement and they have reached the same conclusions.

* Some of the data reported here were presented at the 36th Congress of ANZAAS, August 1962, Sydney.

† Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, Maribyrnong, Vic.

[1] Freeman, J. P., *J. Amer. Chem. Soc*, 1958, **80**, 5954.

[2] Okawara, R., Webster, D. E., and Rochow, E. G., *J. Amer. Chem. Soc.*, 1960, **82**, 3287.

[3] Okawara, R., and Sato, H., *J. Inorg. Nucl. Chem.*, 1961, **16**, 204.

[4] Beattie, I. R., and Gilson, T., *J. Chem. Soc.*, 1961, 2585.

[5] van der Kerk, G. J. M., Luijten, J. G. A., and Janssen, M. J., *Chimia*, 1962, **16**, 10.

[6] Luijten, J. G. A., Janssen, M. J., and van der Kerk, G. J. M., *Rec. Trav. Chim. Pays-Bas*, 1962, **81**, 707.

[7] Beattie, I. R., McQuillan, G. P., and Hulme, R., *Chem. & Ind.*, 1962, 1429.

[8] Okawara, R., Hathaway, B. J., and Webster, D. E., *Proc. Chem. Soc.*, 1963, 13.

[9] Hathaway, B. J., and Webster, D. E., *Proc. Chem. Soc.*, 1963, 14.

[10] Poller, R. C., *J. Inorg. Nucl. Chem.*, 1962, **24**, 593.

[11] Janssen, M. J., Luijten, J. G. A., and van der Kerk, G. J. M., *Rec. Trav. Chim. Pays-Bas*, 1963, **82**, 90.

TABLE 1

TRIBUTYLTIN CHLOROACETATES AND SODIUM CHLOROACETATES

Compound	Yield (%)	Melting Point	Sn Calculated (%)	Sn Found (%)	Cl Calculated (%)	Cl Found (%)	Frequency, ν_1 (COO^- *sym*, cm^{-1})	Frequency, ν_2 (COO^- *asym*, cm^{-1})	Band Separation $\nu_2-\nu_1$
Tributyltin acetate	80	84·5°	34·0	34·2	—	—	1417	1570	153
Sodium acetate	—	—	—	—	—	—	1440	1576	136
Tributyltin monochloroacetate	72	46–47°	30·9	30·3	9·3	9·2	1404	1596	192
Sodium monochloroacetate	—	—	—	—	—	—	1418	1598	180
Tributyltin dichloroacetate	78	50–51°	28·3	27·5	16·9	17·1	1364	1627	263
Sodium dichloroacetate	—	—	—	—	—	—	1395	1646	241
Tributyltin trichloroacetate	73	80·5°	26·1	25·9	23·5	23·9	1340	1646	306
Sodium trichloroacetate	—	—	—	—	—	—	1352	1672	320

Discussion

Beattie and Gilson[4] have shown from an infrared study of methyltin acetates, that an acetate group which was acting as a chelate or bridging group in a covalent compound would be expected to show C=O stretching frequencies very similar to those of an ionic acetate.

The significance of the degree of separation of the two C=O stretching frequencies was studied by Poller,[10] and we have now extended this work to a series of substituted

Table 2

TRIBUTYLTIN ALIPHATIC ESTERS, $(C_4H_9)_3SnOOCR$

Compound	Melting Point or Boiling Point	n_D^{20}	Sn Calc. (%)	Sn Found (%)	State	Carboxyl/Carbonyl Frequency (cm^{-1})	
Tributyltin formate	120–125°/0·7 mm	1·4942	35·5	35·2	Liquid	1580	—
Tributyltin acetate	84·5°	—	34·0	34·2	Solid	1570	—
Tributyltin propionate	69–70°	—	32·7	33·1		1570	—
Tributyltin butyrate	67–68°	—	31·5	31·6		1580	—
Tributyltin valerate	62°	—	30·4	30·6		1560	—
Tributyltin caproate	47°	—	29·3	29·1		1570	—
Tributyltin heptylate	56°	—	28·3	28·6		1560	—
Tributyltin caprylate	47°	—	27·4	26·7		1560	—
Tributyltin pelargonate	43–44°	—	26·6	26·3	Semisolid	1560	1635sh*
Tributyltin caprate	160–161°/2 mm	1·4815	25·7	25·5	Liquid	1555	1644
Tributyltin undecylate	167–169°/2 mm	1·4801	25·0	24·8		1555	1644
Tributyltin laurate	180–182°/2 mm	1·4825	24·3	24·2		1555	1644
Tributyltin tridecylate	—	1·4785	23·6	23·2		1555	1644
Tributyltin myristate	—	1·4792	23·0	23·1		1555	1644
Tributyltin pentadecylate	—	1·4782	22·4	22·5		1555	1643
Tributyltin palmitate	—	1·4798	21·8	21·6		1550	1642
Tributyltin margarate	—	1·4774	21·2	21·1		1555	1645
Tributyltin stearate	18–23°	1·4778	20·7	20·6	Semisolid	1555	1642
Monobutyl (tributyltin) phthalate	200°/0·5 mm	1·5121	23·2	23·7	Liquid	1570	1650
Tributyltin methacrylate	18°	1·4811	31·7	31·3		—	1720 1620sh
Polytributyltin methacrylate	—	—	31·7	31·5	Elastic solid	1570 sh	1640
Tributyltin acrylate	75°	—	32·9	32·5	Semi-solid	1545	—
Polytributyltin acrylate	—	—	32·9	32·7		1570 sh	1640

* sh, shoulder.

tributyltin acetates. As shown in Table 1 the difference between the asymmetric and symmetric carboxyl stretching frequencies for tributyltin acetate, monochloroacetate, dichloroacetate, and trichloroacetate is of the same order as that for the corresponding sodium salts of the acids.

The band separations increase with increasing acid strength while the band frequencies of the tributyltin esters and the sodium salts of the acids in the

1500–1700 cm^{-1} region are similar. The low melting point, or liquid nature, of the tributyltin carboxylates as well as their solubility in light petroleum suggests that they are essentially covalent compounds containing bidentate carboxyl groups, rather than ionic compounds.

As shown in Table 2, all the solid esters from tributyltin acetate to caprylate exhibit a strong band near 1570 cm^{-1}, which corresponds closely to a similar band in sodium acetate, and may be assigned to the COO^- asymmetric stretching vibration. On melting, this band disappears and is replaced by another band near 1640 cm^{-1}. The change in spectra on melting for tributyltin butyrate is shown in Figure 1. This shift is considered too large to be due to a change of state and it is more reasonable to assign the band near 1640 cm^{-1} to a normal carbonyl vibration. The frequency shift from the normal ester range can be attributed to the influence of the metal atom. Similar band shifts due to the influence of metal atoms such as Si, Ge, Sn, and Pb have been reported by Noltes, Henry, and Janssen.[12]

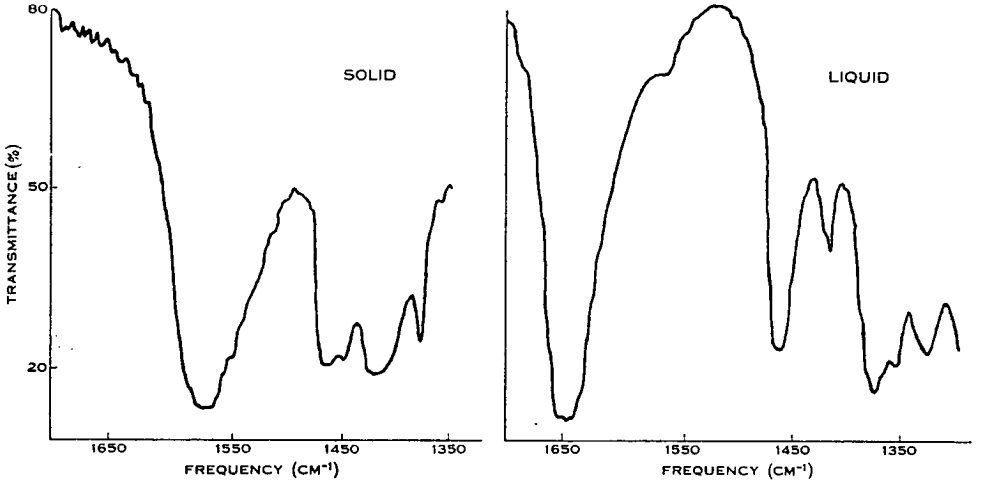

Fig. 1.—Effect of melting on the infrared spectrum of tributyltin butyrate.

The presence of carbonyl vibrations due to different type ester groups in an organotin compound is shown in Figure 2 for monobutyl (tributyltin) phthalate. This spectrum shows near 1730 cm^{-1} the normal C=O stretching frequency due to the $-COOC_4H_9$ group and near 1650 cm^{-1} the C=O stretching frequency due to the $-COOSn(C_4H_9)_3$ group. In the melts of the solid esters the shape of the band envelope near 1640 cm^{-1}, and modifications of the spectrum in the 1400–1450 cm^{-1} region, are typical of a carbonyl rather than a carboxyl group. In dilute solutions in nonpolar solvents all the solid tributyltin carboxylates exhibit only the 1640 cm^{-1} band.

All the liquid esters from tributyltin pelargonate to tributyltin stearate at room temperature exhibit two bands in the 1500–1700 cm^{-1} region: a strong band near 1550 cm^{-1} and a weaker band near 1640 cm^{-1}. Details of the bands are given in

[12] Noltes, J. G., Henry, M. C., and Janssen, M. J., *Chem. & Ind.*, 1959, 298.

Table 2. The spectrum of the liquid ester tributyltin formate like that for trimethyltin formate as reported by Okawara, Webster, and Rochow[2] is anomalous.

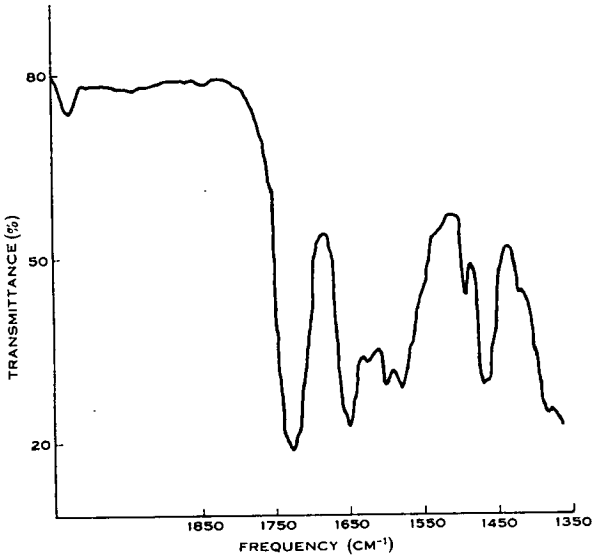

Fig. 2.—Infrared spectrum of monobutyl(tributyltin)phthalate showing C=O absorption bands at 1720 and 1650 cm^{-1}.

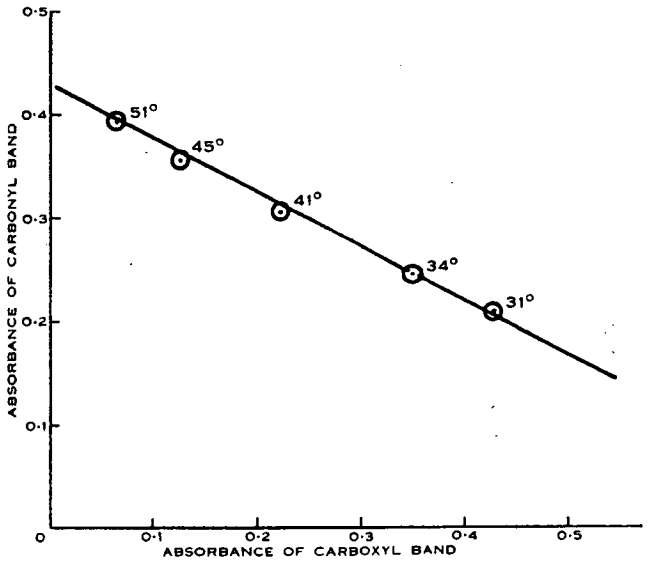

Fig. 3.—Effect of temperature on band intensities of tributyltin laurate.

Although the band near 1550 cm^{-1} in the liquid esters could be due to liquid crystallinity, microscopic examination failed to find any evidence of a mesophase.

On heating the liquid esters to about 70° the band near 1550 cm^{-1} vanished, and the 1640 cm^{-1} band increased in intensity. This change in intensity indicates the presence of an equilibrium between the carbonyl band at 1640 cm^{-1} and the carboxyl band at 1550 cm^{-1}. Band intensity measurements of an 80% solution of tributyltin laurate in carbon tetrachloride over the temperature range 31–55° show that an equilibrium exists and the plot is shown in Figure 3.

It is unlikely that the carboxylate ion would persist in the liquid state at the same time as the ester form unless some type of stabilizing mechanism was present. A simple stabilization mechanism would be chelation to the tributyltin group. It would appear therefore that in the solid state the carboxylates exist as chelate compounds and this structure persists in the carboxylates that are liquid at room temperature. The chelate structure is broken down to the ester form by heat or by solution.

The infrared spectra of tributyltin methacrylate and acrylate monomers in the 1500–1700 cm^{-1} region are similar to the spectra of other tributyltin carboxylates with minor modifications due to the conjugation between the C=C bond and the C=O bond. The monomers on polymerization to high molecular weight, elastic solids, partially soluble in ketonic solvents and insoluble in water, have properties more consistent with ester-type covalent polymers than with ionic polymers. The presence of a shoulder at 1570 cm^{-1} in the spectra of the polymers indicates that some chelation between the carbonyl groups pendant to the vinyl chains of the polymer may exist.

Experimental

Infrared spectra were recorded on a Perkin–Elmer model 125 spectrometer using a spectral slit width of about 2 cm^{-1}. Samples were either in the form of melts, capillary films, or as dilute solutions in carbon tetrachloride. Melting points are uncorrected and tin was determined according to the method of Luijten and van der Kerk.[13]

All esters were prepared by a similar procedure, and the method described for the preparation of tributyltin monochloroacetate is typical. Liquid esters were purified by distillation under vacuum or, in the case of those with higher boiling points, by washing with light petroleum (b.p. 40–70°) at −60°. Solid esters were recrystallized from light petroleum at −20°, filtered, and dried under vacuum at room temperature. In all cases yields of esters greater than 70% were obtained. Details of the esters prepared are given in Tables 1 and 2.

Tributyltin Monochloroacetate.—Bis(tributyltin)oxide, b.p. 180°/1 mm, n_D^{20} 1·4868 (59·6 g; 0·1 mole) in a 250 ml round-bottomed flask was slowly treated, at room temperature, with recrystallized monochloroacetic acid (18·9 g; 0·2 mole). The flask was then heated on an oil-bath at 105–110° for 0·5 hr to drive off water formed in the reaction. After drying under vacuum (10–15 mmHg) at 70° for 1 hr the product was allowed to cool and solidify. The powdered solid was dissolved in light petroleum (250 ml) and cooled overnight at −20°. The filtered crystals were dried under vacuum to give the product as fine needles; m.p. 46–47°, in a yield of 72% (Found: Sn, 30·3; Cl, 9·2%. Calc. for $C_{14}H_{29}ClO_2Sn$: Sn, 30·9; Cl, 9·3%).

Monobutyl(tributyltin) Phthalate.—Bis(tributyltin)oxide (59·6 g; 0·1 mole) and monobutyl phthalate (44·4 g; 0·2 mole) were heated together on an oil-bath at 110° for 0·5 hr. After drying under vacuum the crude material was distilled, b.p. 200°/0·5 mm, n_D^{20} 1·5123, to give the product in a yield of 84% (Found: Sn, 23·7%. Calc. for $C_{24}H_{40}O_4Sn$: Sn, 23·2%).

[13] Luijten, J. G. A., and van der Kerk, G. J. M., "Investigations in the Field of Organotin Chemistry." (Tin Research Institute: England 1955.)

Tributyltin acetate was prepared by the method of Luijten and van der Kerk[12] while tributyltin laurate was a commercial material. Tributyltin octanoate (caprylate) has also been prepared by Alleston and Davies.[14] Tributyltin methacrylate and acrylate were prepared and polymerized by the method of Montermoso, Andrews, and Marinelli.[15]

ACKNOWLEDGEMENTS

The assistance of Mr. T. Norris with the preparation of many of the compounds listed is acknowledged. This paper is published with the permission of the Chief Scientist, Australian Defence Scientific Service, Department of Supply, Melbourne.

[14] Alleston, D. L., and Davies, A. G., *J. Chem. Soc.*, 1962, 2050.
[15] Montermoso, J. C., Andrews, T. M., and Marinelli, L. P., *J. Polym. Sci.*, 1958, **32**, 523.

APPENDIX 10 INFRARED STUDIES ON ORGANOTIN COMPOUNDS

10d Preparation, Properties and Structure of Some Organotin Acrylates
R.A. CUMMINS, P. DUNN and D. OLDFIELD
Aust. J. Chem., 24, No. 11, 2257-66 (1971)

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PREPARATION, PROPERTIES, AND STRUCTURE OF SOME ORGANOTIN ACRYLATES*

By R. A. Cummins,† P. Dunn,† and D. Oldfield†

[Manuscript received March 15, 1971]

Abstract

A series of organotin esters of 2-cyano-3,3-diphenylacrylic acid has been prepared. The esters decarboxylated on heating to give the corresponding organotin olefins. The thermal stability, fungicidal activity, and structure of these esters have been investigated.

Introduction

Trialkyl- and triaryl-tin compounds are active fungicides,[1] but are degraded by ultraviolet light to form organotin compounds with markedly reduced fungicidal activity. As substituted cyanoacrylates are known to be effective ultraviolet absorbers,[2] a programme was initiated to synthesize a new class of organotin compounds, which contained both a cyanoacrylate group and a triorganotin group in the one molecule. This report describes the preparation of a series of organotin esters of 2-cyano-3,3-diphenylacrylic acid, their subsequent decarboxylation on heating, and their structure.

Results and Discussion

(*a*) *The Decarboxylation of Organotin Esters*

Previous work by van der Kerk[1] showed that organotin cyanoacetates liberated carbon dioxide on heating to give the corresponding cyanomethyl organotin compounds, for example:

$$R_3SnO_2CCH_2CN \rightarrow R_3SnCH_2CN + CO_2$$

The recently described interfacial condensation method for the preparation of organotin esters[3] was applied to the reaction of the sodium salt of 2-cyano-3,3-diphenylacrylic acid with triorganotin chlorides:

$$R_3SnCl + (C_6H_5)_2C{=}C(CN)CO_2Na \rightarrow (C_6H_5)_2C{=}C(CN)CO_2SnR_3 \quad (1)$$

[R = (a) C_6H_5; (b) CH_3; (c) C_2H_5; (d) n-C_3H_7; (e) n-C_4H_9]

* Presented at the Third Conference of the Coordination and Metal Organic Chemistry Division, Royal Australian Chemical Institute, Canberra, August 17–21, 1970.

† Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, P.O. Box 50, Ascot Vale, Vic. 3032.

[1] Luijten, J. G. A., and van der Kerk, G. J. M., "Investigations in the Field of Organotin Chemistry." (Tin Research Institute: London 1955.)

[2] "Modern Plastics Encyclopedia." Vol. 46, No. 10A, p. 1008. (McGraw–Hill: New York 1969.)

[3] Frankel, M., Gertner, D., Wagner, D., and Zilkha, A., *J. organomet. Chem.*, 1967, **9**, 83.

The esters so prepared were all observed to effervesce vigorously at temperatures above their melting points; the gas evolved was identified as carbon dioxide by its infrared spectrum. The amount of carbon dioxide evolved in each case was found by absorption in soda-lime. All the esters evolved an almost equimolar amount of carbon dioxide on heating to 200°, as required by the equation:

$$\underset{(1)}{(C_6H_5)_2C{=}C(CN)CO_2SnR_3} \rightarrow \underset{(2)}{(C_6H_5)_2C{=}C(CN)SnR_3} + CO_2$$

Differential thermal analysis (d.t.a) and thermogravimetric analysis (d.t.g.) studies were undertaken, and the results for the triphenyltin ester are given in Figure 1.

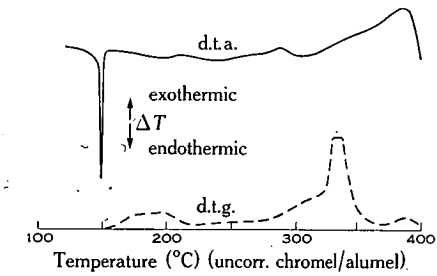

Fig. 1.—The d.t.a. and d.t.g. traces for triphenyltin 2-cyano-3,3-diphenylacrylate (1a).

The upper d.t.a. curve shows a slow endothermic process above the sharp melting point of the ester and this is seen from the lower curve of rate of weight loss to correspond to the evolution of carbon dioxide as is observed visually at this stage. The other organotin esters exhibited similar but more complex traces with much decomposition taking place around 200° due to the thermal instability of the decarboxylation products.

Triphenyltin 2-cyano-3,3-diphenylacrylate (1a) on heating to 200° evolved carbon dioxide to yield a crystalline product which was thermally stable at 200° and was identified as (1-cyano-2,2-diphenylethylene)triphenyltin (2a). The infrared spectra of compounds (1a) and (2a) showed a strong nitrile absorption, which was shifted by 40 cm^{-1} to lower frequency on conversion of (1a) into (2a). This shift was found to be typical of the decarboxylated products and together with the absence of the original carboxyl absorption was used as diagnostic evidence that the reaction had gone to completion.

Reaction of (1-cyano-2,2-diphenylethylene)triphenyltin (2a) with methanolic sodium hydroxide resulted in cleavage of the triphenyltin group to form bis(triphenyltin) oxide, and recovery of 1-cyano-2,2-diphenylethylene (3) from the reaction mixture:

$$\underset{(2a)}{(C_6H_5)_2C{=}C(CN)Sn(C_6H_5)_3} + NaOH \rightarrow \underset{(3)}{(C_6H_5)_2C{=}C(CN)H} + [(C_6H_5)_3Sn]_2O$$

This compound (3) was also obtained when sodium 2-cyano-3,3-diphenylacrylate (4) was heated to 250°:

$$\underset{(4)}{(C_6H_5)_2C{=}C(CN)CO_2Na} \rightarrow (C_6H_5)_2C{=}C(CN)H + CO_2$$

Reaction of compound (2a) with bromine in methanol at 0° gave a complex mixture which appeared on the basis of its infrared spectrum and thin-layer chromatogram to contain bromobenzene, a triphenyltin compound, 1-bromo-1-cyano-2,2-diphenylethylene (5), and possibly a diphenyltin compound. This mixture could have been produced by initial cleavage of the triphenyltin residue followed by further bromination:

$$(C_6H_5)_2C{=}C(CN)Sn(C_6H_5)_3 + Br_2 \rightarrow (C_6H_5)_3SnBr + (C_6H_5)_2C{=}C(CN)Br \quad (5)$$

$$(C_6H_5)_3SnBr + Br_2 \rightarrow (C_6H_5)_2SnBr_2 + C_6H_5Br$$

Compound (5) was isolated from another reaction described below and was detected in the present mixture by t.l.c.

T.l.c. was used extensively in the examination of all the reaction mixtures and some typical results are presented in a later section. By using several different eluent systems it was possible to determine the number of components in these mixtures although it did not prove possible to obtain pure samples of each component in most cases.

The trimethyltin ester (1b) was heated to 190° to give, after recrystallization, a material shown by t.l.c. to consist of two components which could not be further separated. The proton n.m.r. spectrum and elementary analysis of the mixture suggested that a disproportionation of the following type could have taken place:

$$2(C_6H_5)_2C{=}C(CN)Sn(CH_3)_3 \rightarrow [(C_6H_5)_2C{=}C(CN)]_2Sn(CH_3)_2 + (CH_3)_4Sn$$

The recrystallized mixture was treated with methanolic iodine to give 1-cyano-1-iodo-2,2-diphenylethylene (6):

$$(C_6H_5)_2C{=}C(CN)Sn(CH_3)_3 + I_2 \rightarrow (C_6H_5)_2C{=}C(CN)I \quad (6)$$

Treatment with methanolic bromine at 0° similarly produced 1-bromo-1-cyano-2,2-diphenylethylene (5) which was used to identify one of the components in the analogous reaction above of the triphenyltin compound:

$$(C_6H_5)_2C{=}C(CN)Sn(CH_3)_3 + Br_2 \rightarrow (C_6H_5)_2C{=}C(CN)Br \quad (5)$$

When the higher trialkyltin esters (1c, 1d, 1e) were heated to 150–200° the resulting liquid residues, on examination of their infrared spectra and by t.l.c., appeared to contain the expected decarboxylation product (2) and also some of the olefin (3). These residues were not purified further; however, the nitrile absorption in their infrared spectra was in the same position as the earlier products from the triphenyl- and trimethyl-tin esters.

(*b*) *Thin-Layer Chromatography*

The mixtures were examined on silica gel GF254 (Merck) using a variety of developing systems and the components were made visible by iodine vapour followed by spraying with 0·1% catechol violet. By this means it was possible to determine which of the components were organotin compounds. For any series of compounds

$R_{4-n}SnX_n$, the R_F value in a given developer is largely independent of the nature of X so that chlorides and bromides have approximately the same R_F value.[4] It is however possible to distinguish between R_2SnX_2 and R_3SnX by t.l.c. Using the developer system, ethanol–sodium acetate, the R_F value for R_2SnX_2 is smaller than for R_3SnX, hence the tentative assignment of an unknown component of the reaction mixture from $Ph_2C{=}C(CN)SnPh_3$ and bromine was made as probably a Ph_2SnX_2 species. Typical results are presented in Table 1.

TABLE 1

R_F VALUES FOR ORGANOTIN COMPOUNDS WITH SPECIFIC DEVELOPING SYSTEMS

Compound or Reaction Mixture	R_F in EtOH–NaOAc[a] 2 : 1	R_F in CCl_4	R_F in EtOH
Ph_3SnCl	0·72	0·50	0·62
$Ph_2C{=}C(CN)H$	0·78	0·07	0·69
$Ph_2C{=}C(CN)Br$	0·80	0·15	0·65
$Ph_2C{=}C(CN)SnPh_3+NaOH$	0·70, 0·79	0·05, 0·47	0·62, 0·69
$Ph_2C{=}C(CN)SnPh_3+Br_2$	0·55, 0·62, 0·75	0·15, 0·24	0·50, 0·65
Me_3SnCl	0·80	0·20	
$Ph_2C{=}C(CN)CO_2SnMe_3$ decarboxylation	0·10, 0·69, 0·75, 0·82	0·06, 0·19	

[a] Sodium acetate solution from sodium acetate (8·2 g) plus glacial acetic acid (5·7 ml) in water (100 ml).

(c) *Structure*

Infrared Spectra

Considerable evidence[5–9] has led to the general conclusion that compounds of the formula $R_3SnOCOR'$ are chelate or pentacoordinate in the solid state and monomeric in the liquid in those cases where R and R′ are simple saturated alkyl or phenyl groups. It has also been shown with some alkyltin esters of fatty acids that these forms can coexist in the liquid state.[10] More recent work has demonstrated that the monomeric form is the stable form in the solid state when R is a bulky group such as cyclohexyl[11] and neophyl[12] and when R′ is a branched-chain alkyl group.[13] These cyanoacrylates, as originally prepared at room temperature, showed carbonyl frequencies near 1650 cm^{-1} (Table 2). This result suggests that all the esters in this series also maintain the ester conformation in the solid state.

However, when the trimethyltin compound was heated on a Kofler hot-stage microscope it was observed to melt and resolidify between 80° and 90° and then to

[4] Bürger, K., *Z. analyt. Chem.*, 1962, **192**, 280.
[5] Luijten, J. G. A., Janssen, M. J., and van der Kerk, G. J. M., *Recl Trav. chim. Pays-Bas*, 1962, **81**, 707.
[6] Beattie, I. R., and Gilson, T., *J. chem. Soc.*, 1961, 2585.
[7] Beattie, I. R., McQuillan, G. P., and Hulme, R., *Chemy Ind.*, 1962, 1429.
[8] Okawara, R., Hathaway, B. J., and Webster, D. E., *Proc. chem. Soc.*, 1963, 13.
[9] Hathaway, B. J., and Webster, D. E., *Proc. chem. Soc.*, 1963, 14.
[10] Cummins, R. A., and Dunn, P., *Aust. J. Chem.*, 1964, **17**, 181.
[11] Alcock, N. W., and Timms, R. E., *J. chem. Soc.* (*A*), 1968, 1876.
[12] Herber, R. H., Stockler, H. A., and Reichle, W. T., *J. chem. Phys.*, 1965, **42**, 2447.
[13] Ford, B. F. E., and Sams, J. R., *J. organomet. Chem.*, 1970, **21**, 345.

melt again with decarboxylation at 167°. The material recovered after the initial melting showed a new carbonyl absorption near 1590 cm^{-1}. Both the frequency and shape of this band was similar to those of the sodium and potassium salts of the parent acid, 2-cyano-3,3-diphenylacrylic acid. The solution spectra in carbon tetrachloride of both the original sample and the melted one were identical—the carbonyl band appearing near 1650 cm^{-1}, the frequency of the ester form. It is believed that these phenomena indicate a thermal conversion of the original monomeric ester form into one containing the pentacoordinate tin atom, and is the first observation of polymorphism in these esters.

TABLE 2

INFRARED FREQUENCIES (cm^{-1})

Compound	Nitrile Region		Carbonyl/Carboxyl Region	
	CCl_4 Solution	Solid	CCl_4 Solution	Solid
$R_3SnO_2CC(CN)C(C_6H_5)_2$				
where R = CH_3	2215	2232	1650	1652
CH_3[a]	2215	2215	1650	1590
C_2H_5	2217	2212	1650	1652
n-C_3H_7	2215	2212	1650	1652
n-C_4H_9	2215	2210	1652	1652
C_6H_5	2220	2212	1640	1645
$R_3SnC(CN)C(C_6H_5)_2$				
where R = CH_3	2175	2170		
C_2H_5	2172	2170		
n-C_3H_7	2172	2175		
n-C_4H_9	2174	2170		
C_6H_5	2177	2175		
$HO_2CC(CN)C(C_6H_5)_2$		2220		
$BrC(CN)C(C_6H_5)_2$		2220[b]		
$HC(CN)C(C_6H_5)_2$		2210		

[a] After heating to 100°.

[b] From Kobrich, G., Trapp, H., and Akhtar, A., *Chem. Ber.*, 1968, **101**, 2644.

None of the other esters underwent any changes on heating to their melting points; the spectra after melting and rapid cooling to preclude decarboxylation were identical to the original. It is apparently only the trimethyltin ester that can exist in the chelate form. Table 2 lists the infrared frequencies observed for the nitrile and carbonyl/carboxyl stretching vibrations of these organotin acrylates, and the nitrile stretching vibrations of their derived olefins and some allied compounds.

The solution spectra of all these organotin esters exhibit the CN stretching frequency near 2215 cm^{-1} at the lower end of the range assigned to α,β-unsaturated olefins.[14a] This demonstrates that any interaction between the carbonyl group and the nitrile group is too small to upset this correlation. This is supported by the frequency of 2220 cm^{-1} observed for the parent acid. Further support still may be adduced by

[14] Bellamy, L. J., "Infrared Spectra of Complex Molecules." 2nd Edn, (*a*) p. 263; (*b*) p. 72. (Methuen: London 1958.)

the nitrile frequency observed for tributyltin cyanoacetate which, being near 2250 cm^{-1}, falls well within the range assigned to saturated nitriles.

However, these frequencies undergo marked changes in the derived olefins. There is a fall of about 40 cm^{-1} to a value near 2175 cm^{-1} for all the organotin olefins, giving the nitrile group a frequency in a range more often associated with the thiocyanate group. That the fall is unlikely to be due to the loss of the carboxyl group is indicated by the nitrile frequency of 1-cyano-2,2-diphenylethylene, which, near 2210 cm^{-1}, is only about 10 cm^{-1} below that of the parent acid. The fall is also unlikely to be due to the hybridization state of the α-carbon atom, since an analogous fall of nearly 30 cm^{-1} occurs between tributyltin cyanoacetate and tributylcyanomethyltin.

Since the tin atom has moved from a position γ to one α to the CN group it would be tempting to ascribe the low frequencies to the mass effect of the tin atom. However, in the light of the most recent discussion[15] of this effect it is unlikely to be the cause. Moreover, the nitrile frequency reported[16] for 1-bromo-1-cyano-2,2-diphenylethylene is near 2220 cm^{-1} and still well within the range of α,β-unsaturated nitriles. It can be concluded therefore that the cause of these large falls is unknown.

The carbonyl frequencies both in the solid state and in solution fall within the range observed for saturated alkyl organotin esters[6] despite the fact that the structures suggest the possibility of both conjugation with the olefinic bond and interaction with the nitrile group. While these effects may both be present and zero, an alternative explanation is that the carbonyl group is out of the plane of the double bond and gauche to the nitrile group. This explanation is supported by the nitrile group frequency being apparently unaffected by the carbonyl.

This may not however be the case for the two solid state forms of the trimethyltin compound. In the ester form the nitrile group exhibits a frequency near 2230 cm^{-1} and in the chelate form one near 2215 cm^{-1}. The carboxyl frequency of the chelate form is near 1595 cm^{-1} which is some 25 cm^{-1} above the range found for saturated alkyl organotin carboxylates and very close to the carboxyl frequency of the sodium salt. It seems likely therefore that at least in the chelate case there is some interaction between the nitrile and carboxyl groups, possibly brought about by the equivalence of the C=O bonds.

However, interpretation of the behaviour of the nitrile frequencies in terms of this interaction is difficult.

That conjugation of the olefinic double bond and the phenyl rings is occurring may be adduced by the strength of the band near 1570 cm^{-1}. This band is the lower member of a doublet and is nearly as intense as the upper member near 1590 cm^{-1}. Both bands are associated with the normal aromatic ring vibrations but it has been concluded[14b] that when the lower member appears as a clearly defined band of medium intensity, external conjugation is probably present. Molecular models suggest that while it is not possible for both aromatic rings to lie in the plane of the olefinic bond, both may adopt positions close enough to the plane to give sufficient π-orbital overlap to satisfy the conditions for conjugation.

[15] Bellamy, L. J., "Advances in Infrared Group Frequencies." 1st Edn, pp. 66–72. (Methuen: London 1968.)

[16] Köbrich, G., Trapp, H., and Akhtar, A., *Chem. Ber.*, 1968, **101**, 2644.

Ultraviolet Spectra

The wavelengths of maximum absorption (λ_{max}) and the extinction coefficient for the absorption in the ultraviolet region of all the esters, in methanol solution, are given in the Experimental section. It is seen that the original intention of retaining the ultraviolet absorbing characteristics of the acrylate group has been achieved and also this property is largely independent of the presence of the organotin group in the molecule or the absence of the carboxyl group.

(*d*) *Fungicidal Activity*

Since the organotin esters prepared should combine the attributes of a fungicide with those of an ultraviolet absorber they were tested for fungicidal activity against a range of ten fungi. The results are shown for each culture in Table 3.

TABLE 3

FUNGICIDAL ACTIVITY OF $R_3SnO_2CC(CN)C(C_6H_5)_2$

Cultures used: 1, *Stemphylium sp.*; 2, *Penicillium notatum*; 3, *Fusarium sp.*; 4, *Paecilomyces varioti*; 5, *Aspergillus flavus*; 6, *Cladosporium resinae*; 7, *Rhizopus stolonifer*; 8, *Mucor sp.*; 9, *Aspergillus niger*; 10, *Chaetomium globosum*. +, Fungal growth; −, no fungal growth

Compound	Concentration (p.p.m.)	Culture No.									
		1	2	3	4	5	6	7	8	9	10
(1a)	1000	−	−	−	−	−	−	−	−	−	−
	100	−	−	−	−	−	−	−	−	−	−
	10	+	+	+	+	+	+	−	+	+	+
	1	+	+	+	+	+	+	−	+	+	+
(1b)	1000	−	−	−	−	−	−	−	−	−	−
	100	+	−	+	+	+	+	+	+	+	+
	10	+	+	+	+	+	+	+	+	+	+
	1	+	+	+	+	+	+	+	+	+	+
(1c)	1000	−	−	−	−	−	−	−	−	−	−
	100	−	−	−	−	−	−	−	−	−	−
	10	−	+	−	−	−	−	−	+	−	−
	1	+	+	+	+	+	+	−	+	+	+
(1d)	1000	−	−	−	−	−	−	−	−	−	−
	100	−	−	−	−	−	−	−	−	−	−
	10	−	−	−	−	−	−	−	+	−	−
	1	+	+	+	+	+	+	−	+	+	−
(1e)	1000	−	−	−	−	−	−	−	−	−	−
	100	−	−	−	−	−	−	−	−	−	−
	10	+	−	+	+	+	+	−	+	+	−
	1	+	+	+	+	+	+	−	+	+	−
(2a)	1000	+	+	+	+	+	+	+	+	+	+
	100	+	+	+	+	+	+	+	+	+	+
	10	+	+	+	+	+	+	+	+	+	+

The most active compounds were the triethyltin and tripropyltin esters, which were both effective in preventing growth of all fungi when they were present at a concentration of 10 p.p.m. in the agar medium. A slightly lower activity was found for the tributyltin and triphenyltin esters; however, a concentration of 100 p.p.m. of these

organotin compounds was sufficient to prevent growth of all the test fungi. As shown in Table 3 the decarboxylated triphenyltin ester (2a) was completely inactive in preventing fungal growth. These results are in accordance with the earlier work by van der Kerk on the fungicidal properties of organotin compounds.[1]

Experimental

(a) *General*

All melting points are uncorrected and were determined on a Kofler hot-stage microscope. Infrared spectra were recorded on a Perkin–Elmer 125 spectrophotometer; the frequencies are correct to within 2 cm^{-1} in the 2200 cm^{-1} region and to within only 5 cm^{-1} in the 1600 cm^{-1} region, principally because of the difficulty in picking the band centre. Ultraviolet spectra of solutions in methanol were recorded on an Unicam SP800 spectrophotometer. Microanalyses were performed by Australian Microanalytical Service, Melbourne.

The differential thermal analyses were performed on a DuPont 900 differential thermal analyser using a heating rate of 1·75°/min. The DSC cell was used with the sample (2–4 mg) contained in an open aluminium pan.

A Stanton HT-SM automatic thermorecording balance was used for the thermogravimetric work. The derivative trace was obtained directly from a velocity transducer attached to the shaft carrying the recorder pen. The sample (200–300 mg) was contained in an open platinum crucible and the heating rate used was 1·75°/min.

(b) *Preparation of Organotin Esters*

Materials

2-Cyano-3,3-diphenylacrylic acid was obtained from hydrolysis of its 2-ethylhexyl ester, Uvinul N539 (GAF Corp., New York), with alcoholic potassium hydroxide. The organotin chlorides were used as supplied by the manufacturer (M&T Chemicals Inc., Rahway, N.J.).

All the esters were prepared by a similar procedure and the method described for trimethyltin 2-cyano-3,3-diphenylacrylate is typical.

Trimethyltin 2-Cyano-3,3-diphenylacrylate

2-Cyano-3,3-diphenylacrylic acid (4·0 g; 16 mmol) was suspended in water (100 ml) and neutralized to phenolphthalein with 0·2N NaOH. Trimethyltin chloride (3·2 g; 16 mmol) in n-hexane (150 ml) was added to the rapidly stirred solution, producing immediately a copious white precipitate. The mixture was stirred for 4 hr, filtered, the precipitate washed well with water, dried in a desiccator, and recrystallized from carbon tetrachloride to give colourless plates of *trimethyltin 2-cyano-3,3-diphenylacrylate* (1b) (3·7 g; 9·0 mmol), m.p. 167°, λ_{max} 293 nm (ϵ 11600) (Found: C, 55·3; H, 4·5; Sn, 28·5. $C_{19}H_{19}NO_2Sn$ requires C, 55·3; H, 4·6; Sn, 28·9%).

Other Esters

Similarly prepared were: *triethyltin 2-cyano-3,3-diphenylacrylate* (1c), colourless crystals from hexane, m.p. 144–146°, λ_{max} 291 nm (ϵ 12200) (Found: C, 58·2; H, 5·5; Sn, 26·6. $C_{22}H_{25}NO_2Sn$ requires C, 58·2; H, 5·5; Sn, 26·2%). *Tri-n-propyltin 2-cyano-3,3-diphenylacrylate* (1d), colourless crystals from hexane, m.p. 106–107°, λ_{max} 291 nm (ϵ 11500) (Found: C, 60·0; H, 6·3; Sn, 23·9. $C_{25}H_{31}NO_2Sn$ requires C, 60·5; H, 6·3; Sn, 23·9%). *Tri-n-butyltin 2-cyano-3,3-diphenylacrylate* (1e), colourless crystals from hexane, m.p. 80–81°, λ_{max} 293 nm (ϵ 14500) (Found: C, 62·2; H, 7·0; Sn, 22·3. $C_{28}H_{37}NO_2Sn$ requires C, 62·5; H, 6·9; Sn, 22·1%). *Triphenyltin 2-cyano-3,3-diphenylacrylate* (1a), colourless crystals from hexane, m.p. 144–145°, λ_{max} 293 nm (ϵ 13500) (Found: C, 67·9; H, 4·3; Sn, 20·1. $C_{34}H_{25}NO_2Sn$ requires C, 68·2; H, 4·2; Sn, 19·9%).

(c) *Decarboxylations*

Products

Triphenyltin 2-cyano-3,3-diphenylacrylate (1a) (0·41 g; 0·68 mmol) was decarboxylated by heating at 200° in a stream of nitrogen, the CO_2 evolved being absorbed and weighed. The

colourless residue crystallized from carbon tetrachloride as colourless crystals of *(1-cyano-2,2-diphenylethylene)triphenyltin* (2a), m.p. 146° (0·23 g; 0·42 mmol), λ_{max} 290 nm (ϵ 14900) (Found: C, 70·9; H, 4·9. $C_{33}H_{25}NSn$ requires C, 71·5; H, 4·5%).

Trimethyltin 2-cyano-3,3-diphenylacrylate (1b) was decarboxylated in a similar way to give a *solid* which gave colourless crystals from carbon tetrachloride, m.p. 150–154° (Found: C, 69·7; H, 4·8. $C_{18}H_{19}NSn$ requires C, 58·7; H, 5·2%). T.l.c. showed the crystals to be a mixture of two components with similar R_F values. Proton n.m.r. showed two types of methyl protons linked to tin in approximately equal proportions.

Pyrolysis of sodium 2-cyano-3,3-diphenylacrylate gave a white solid on the cooler parts of the tube which was recrystallized from hexane as white crystals, m.p. 38–40°, cited[17] m.p. 49–50°, for 1-cyano-2,2-diphenylethylene.

The other organotin esters (1c, 1d, 1e) gave intractable liquid residues which were not purified further.

Carbon Dioxide Determinations

The results were as follows. Ester (1a): sample size 0·80 mmol, CO_2 absorbed 0·71 mmol. Ester (1b): 1·08, 1·08. Ester (1c): 0·66, 0·71. Ester (1d): 0·47, 0·45. Ester (1e): 0·58, 0·58.

(*d*) *Reactions of Decarboxylation Products*

Hydrolysis of (1-Cyano-2,2-diphenylethylene)triphenyltin

(1-Cyano-2,2-diphenylethylene)triphenyltin (1·0 g) in methanol (150 ml) and sodium hydroxide (1·0 g) in water (30 ml) were heated together under reflux for 37 hr. Most of the methanol was then distilled out of the solution, water (100 ml) was added and the solution was extracted with ether (2 × 150 ml). The ether layers were combined, dried ($MgSO_4$), and the ether distilled to leave an oily residue containing a light yellow solid. The infrared spectrum of the residue suggested that it contained bis(triphenyltin) oxide[18,19] and also 1-cyano-2,2-diphenylethylene (ν_{CN} 2210 cm^{-1}). Recrystallization from hexane gave colourless crystals (3·0 mg), m.p. 38°, with an infrared spectrum identical to that of the 1-cyano-2,2-diphenylethylene obtained above.

Bromination of (1-Cyano-2,2-diphenylethylene)triphenyltin

Bromine (0·1 ml; 1·8 mmol) was added dropwise to (1-cyano-2,2-diphenylethylene)-triphenyltin (0·5 g; 0·9 mmol) in methanol (200 ml) at 0°, in the dark. The solution was stirred rapidly at this temperature for 10 hr then allowed to attain room temperature. The solvent was distilled on a water-bath to leave a brown oil. The infrared spectrum and t.l.c. of this residue showed an absence of starting material (ν_{CN} 2210 cm^{-1}) and suggested the presence of bromobenzene and 1-bromo-1-cyano-2,2-diphenylethylene. The mixture could not be further purified.

Iodination of the Decarboxylation Product from Trimethyltin 2-Cyano-3,3-diphenylacrylate

The recrystallized product (0·6 g) and iodine (0·4 g) were stirred together in methanol (150 ml) at room temperature for 8 hr, then allowed to stand for 170 hr. The solution was then decolourized with aqueous sodium thiosulphate, ether (250 ml) was added, and the ether layer then washed with water (2 × 150 ml), dried ($MgSO_4$), and the ether distilled to leave a light brown solid. This was recrystallized from hexane as yellow crystals of *1-cyano-1-iodo-2,2-diphenylethylene* (6) (0·25 g), m.p. 115–120° (Found: C, 54·5; H, 3·1. $C_{15}H_{10}IN$ requires C, 54·4; H, 3·0%). The infrared spectrum and proton n.m.r. were consistent with this structure.

Bromination of the Decarboxylation Product from (1-Cyano-2,2-diphenylethylene)triphenyltin

Bromine (0·3 ml, 5·4 mmol) was added dropwise to the recrystallized product (2·0 g) in methanol (100 ml) at 0° in the dark with rapid stirring. The solution was stirred at this temperature for 1 hr, then it was allowed to attain room temperature and the solvent was distilled off to leave a brown oil. Recrystallization from hexane gave colourless crystals (0·3 g), m.p. 88–90°. Elementary

[17] Runti, C., and Sindellari, L., *Chem. Abstr.*, 1961, **55**, 10468.

[18] Kushlefsky, B., Simmons, I., and Ross, A., *Inorg. Chem.*, 1963, **2**, 187.

[19] Cummins, R. A., *Aust. J. Chem.*, 1965, **18**, 98.

analysis suggested the product was 1-bromo-1-cyano-2,2-diphenylethylene, containing some hexane (Found: C, 60·6; H, 5·5. $C_{15}H_{10}BrN$ requires C, 63·4; H, 3·5%). The proton n.m.r. and infrared spectrum were consistent with the structure proposed.

(e) Fungicidal Activity of Organotin Compounds

The organotin compound was dissolved in acetone and aliquots of this solution were added to hot molten potato dextrose agar. The acetone boiled away to leave the organotin compound suspended in the agar at the required concentration. The agar was poured into Petri dishes (110 mm diam.) to a depth of 2–3 mm and allowed to cool and solidify. Ten test fungi were used for the evaluation of each organotin compound.

Inoculation of the cultures at equal intervals around the Petri dish was undertaken by pipetting a dense aqueous suspension of the spores (0·1 ml) to the allocated spot. Control plates consisted of agar with acetone but no organotin compound. All plates were incubated at 30°, examined daily, and assessed after 5 days.

Acknowledgments

The authors are grateful to Dr B. C. Ennis and Mr F. J. Upsher, for the thermal analytical data and for the assessment of fungicidal activity, respectively, and to Dr A. G. Moritz for critical discussion of the spectral data.

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TRIBUTYLTIN ISOTHIOCYANATE AND ISOCYANIDE

By R. A. Cummins and P. Dunn

Appendix 10e

10.56 - 10.64

TRIBUTYLTIN ISOTHIOCYANATE AND ISOCYANIDE*

By R. A. CUMMINS† and P. DUNN†

[*Manuscript received October* 9, 1963]

Summary

Infrared evidence has been used to demonstrate that tributyltin isothiocyanate is formed when certain tributyltin compounds are reacted with inorganic thiocyanates or thiourea. Molecular refraction data supporting this contention are also reported.

The preparation of tributyltin isothiocyanate by several different methods and of tributyltin succinimide is described.

INTRODUCTION

Tributyltin (iso)thiocyanate‡ could have the normal thiocyanate structure, –SCN, or the isothiocyanate structure, –NCS. Although several di- and triaklyltin (iso)thiocyanates have been reported, the structure of these compounds has not been studied.

The first organotin (iso)thiocyanate, diethyltin di(iso)thiocyanate, was prepared by Cahours[1] 100 years ago. Since then Seyferth and Rochow[2] have prepared dimethyl and dibutyltin di(iso)thiocyanates and Seyferth and Stone[3] have prepared divinyltin di(iso)thiocyanate.

Triethyltin (iso)thiocyanate has been prepared by Anderson,[4] and Anderson and Vasta[5] and recently Seyferth and Kahlen[6] prepared trimethyltin (iso)thiocyanate.

Several organotin (iso)cyanides have been reported following the initial preparation of triethyltin (iso)cyanide by Cahours.[7] Seyferth and Kahlen[6,8] have studied the structure of trimethyltin (iso)cyanide and Luijten and van der Kerk[9,10] have prepared tributyltin (iso)cyanide, but the structure of this compound has not been investigated.

* Some of the data reported here were presented at the 36th Congress of A.N.Z.A.A.S., Sydney, August 1962, and at the 4th Australian Spectroscopy Conference, Canberra, August, 1963.

† Defence Standards Laboratories, Maribyrnong, Vic.

‡ The "(iso)thiocyanate" and "(iso)cyanide" nomenclature used in this paper has no structural implications when the iso prefix is in parentheses and merely indicates the presence of the –NCS (or –SCN) and –CN (or –NC) grouping.

[1] Cahours, A., *Liebigs Ann.*, 1862, **122**, 48.

[2] Seyferth, D., and Rochow, E. G., *J. Amer. Chem. Soc.*, 1955, **77**, 1302.

[3] Seyferth, D., and Stone, F. G. A., *J. Amer. Chem. Soc.*, 1957, **79**, 515.

[4] Anderson, H. H., *J. Org. Chem.*, 1954, **19**, 1766.

[5] Anderson, H. H., and Vasta, J. A., *J. Org. Chem.*, 1954, **19**, 1300.

[6] Seyferth, D., and Kahlen, N., *J. Org. Chem.*, 1960, **25**, 809.

[7] Cahours, A., *Liebigs Ann.*, 1860, **114**, 364.

[8] Seyferth, D., and Kahlen, N., *J. Amer. Chem. Soc.*, 1960, **82**, 1080.

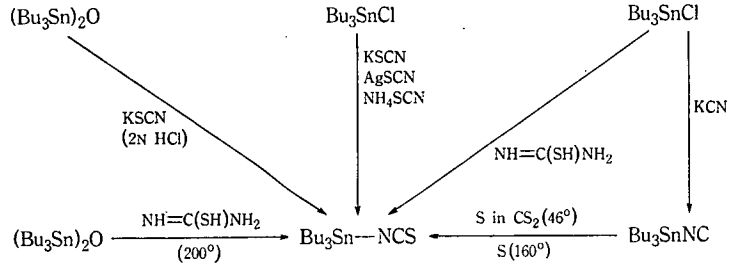
[9] Luijten, J. G. A., and van der Kerk, G. J. M., *J. Appl. Chem.*, 1956, **6**, 49.

[10] Luijten, J. G. A., and van der Kerk, G. J. M., "Investigations in the Field of Organotin Chemistry." (Tin Research Institute: London 1955.)

Tributyltin Isothiocyanate

(a) *Chemical Data*

We have prepared tributyltin (iso)thiocyanate by several different methods, as shown below:



It has been shown[11] that use of silver thiocyanate, in organic reactions, usually leads to the formation of isothiocyanates. Potassium, ammonium, and silver thiocyanates all react with tributyltin chloride, and potassium thiocyanate with

Table 1

Reaction of thiourea compounds with tributyltin (TBT) compounds

Reaction No.	Thiourea Compound	TBT Compound	Product	Yield (%)	By-product	Yield (%)
1	unsubstituted	chloride	TBT (iso)thiocyanate	16	ammonium chloride	—
					TBT chloride (unchanged)	59
2	unsubstituted	oxide	bis-TBT sulphide	70	urea compound	—
			TBT (iso)thiocyanate	15	ammonia	20
3	*NN'*-diphenyl	oxide	bis-TBT sulphide	60	*NN'*-diphenylurea	86
4	*NN'*-diethyl	oxide	bis-TBT sulphide	96	*NN'*-diethylurea	87
5	*NN'*-dibutyl	oxide	bis-TBT sulphide	87	*NN'*-dibutylurea	80

tributyltin oxide, to form the same compound which could be an isothiocyanate. Sowerby[12] has also found, using infrared frequency measurements, that use of ammonium or potassium thiocyanate with various organophosphorus, silicon, and arsenic chlorides leads to complete substitution of chloride groups and the formation of isothiocyanates.

Gilman, Hofferth, and Melvin[13] have shown by chemical means that organosilicon isothiocyanates are formed by the reaction of organosilicon chloride with either ammonium thiocyanate or thiourea. Tributyltin chloride will also react with thiourea to give tributyltin (iso)thiocyanate in low yields (Table 1, reaction 1).

Thiourea will also react with tributyltin oxide to give tributyltin (iso)thiocyanate and tributyltin sulphide, with ammonia and water as reaction by-products.

[11] Anderson, H. H. "Silicon, Sulphur and Phosphorus." Colloquium of the Section for Inorganic Chemistry of I.U.P.A.C., Munster 1954, pp. 37, 235.

[12] Sowerby, D. B., *J. Inorg. Nucl. Chem.*, 1961, **22**, 205.

[13] Gilman, H., Hofferth, B., and Melvin, H. W., *J. Amer. Chem. Soc.*, 1950, **72**, 3045.

In this reaction tributyltin isothiocyanate would be formed if reaction occurred at the imino nitrogen of thiourea as shown in the reaction scheme. The main product from this reaction is tributyltin sulphide, formed by an interchange reaction between oxygen and sulphur (Table 1, reaction 2). Substituted thioureas such as diphenyl, diethyl, and dibutyl thiourea (Table 1, reactions 3, 4, and 5) react with tributyltin oxide to give good yields of tributyltin sulphide. Very little (iso)thiocyanate compound could be detected in these reactions.

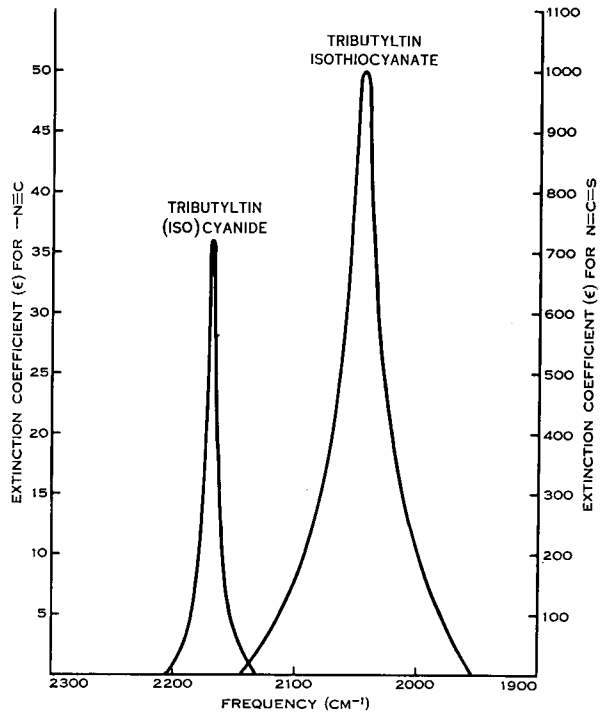


Fig. 1.—Infrared spectra of tributyltin isothiocyanate and tributyltin (iso)cyanide.

Bacon[14] has stated that isothiocyanates generally are more stable than thiocyanates, and that isothiocyanates are often formed by heating thiocyanates. Tributyltin (iso)thiocyanate is a stable compound and heating under vacuum at 180° produced no change in the boiling point, refractive index, or infrared spectrum.

(*b*) *Infrared Data*

Over the range 4000–400 cm^{-1} the main bands in the infrared spectrum of tributyltin (iso)thiocyanate are those characteristic of tributyltin compounds; there are none that can be reasonably assigned to the Sn–N bond. A strong band does occur near 2032 cm^{-1} (Fig. 1) but published data[15] are not sufficiently precise for this

[14] Bacon, R. G. R., "Organic Sulphur Compounds." Vol. 1, p. 311. (Pergamon Press: London 1961.)

[15] Bellamy, L. J., "The Infra-red Spectra of Complex Molecules." 2nd Ed. p. 347. (Methuen: London 1958.)

band to be assigned to either the –SCN or the –NCS structure. However, there is evidence that in covalent compounds the intensity of the –NCS group is from 50 to 100 times stronger than that of the –SCN group in corresponding compounds[16–18] and the properties of tributyltin (iso)thiocyanate indicate that the compound is essentially covalent.

Table 2 lists intensity and frequency data of bands assigned to the –NCS group in several compounds and in a range of solvents. The results show that the band in tributyltin (iso)thiocyanate has an intensity comparable to similar bands in alkyl and aryl isothiocyanates. Moreover the shift to higher frequencies with increasing polarity of solvent closely parallels the behaviour of organic isothiocyanates. This behaviour is not characteristic of the thiocyanate group which is almost insensitive to solvent and suffers only a very small shift to lower frequencies for the same solvent order.

TABLE 2
INFRARED INTENSITY (I) AND FREQUENCY (ν) DATA
ON ORGANTOIN AND ALKYL AND ARYL COMPOUNDS
I in 10^4 mole^{-1} litre cm^{-2}; ν in cm^{-1}, for the band assigned to the –NCS group

Solvent	Bu_3SnNCS		C_6H_5NCS		CH_3NCS		$(NH_4)^+(SCN)^-$		Bu_3SnNC	
	I	ν	I	ν	I	ν	I	ν	I	ν
n-Hexane	10·2	2027	14·8	2045	8·7	2100				
Cyclohexane	9·2	2027	13·1	2044	8·4	2100				
Carbon tetrachloride	10·0	2032	14·2	2051	8·6	2103			0·076	2165
Benzene	10·5	2043	14·6	2073	8·0	2112				
Chloroform	10·5	2056	14·1	2085	8·8	2121				
Acetone	8·8	2053	13·5	2085	7·2	2120	4·9	2055		
Nitromethane	9·6	2058	13·7	2107	7·1	2120				
Water							4·3	2063		

The changes in intensity in the different solvents are quite small and of a similar order to the changes in the organic isothiocyanates. This behaviour also is not characteristic of organic thiocyanates which exhibit a threefold intensity change in the same range of solvents.[18]

Further support for the contention that the tributyltin compound is an isothiocyanate is derived from measurements on ammonium thiocyanate when dissolved in water and acetone. As shown in Table 2 the intensity of the thiocyanate ion is only one-half that of tributyltin (iso)thiocyanate. Even if the tin compound was 100% ionic the intensity of the band would be expected to be much the same as that derived from ammonium thiocyanate. However, it is evident that tributyltin (iso)thiocyanate is essentially covalent, and thus the covalent bonding through the sulphur to the tin atom would be expected to lower the band intensity towards that

[16] Caldow, G. L., and Thompson, H. W., *Spectrochim. Acta*, 1958, **13**, 212.
[17] Ham, N. S., and Willis, J. B., *Spectrochim. Acta*, 1960, **16**, 279.
[18] Cummins, R. A., unpublished data, 1963.

of an organic thiocyanate. Bonding through the nitrogen would be expected to raise the intensity into the region found for organic isothiocyanates. Hence, it may be concluded that the tin compound is more nearly represented by the name tributyltin isothiocyanate.

(c) *Molecular Refraction Data*

When refraction data for organotin compounds reported by Vogel and coworkers[19,20] are used, the bond refractions (Sn–S) and (Sn–N), calculated from tributyltin sulphide and tributyltin succinimide, are found to be 8·30 and 4·02. These values appear reasonable by comparison with the bond refraction values (Si–S), (Si–N), (Ge–S), and (Ge–N) as reported by Vogel, Cresswell, and Leicester.[20] Molecular refraction, R_M (observed), values for tributyltin (iso)thiocyanate and triethyltin (iso)thiocyanate determined from refractive index and density measurements, and R_M (calculated) values for the same compounds based on the above bond refraction values are given in Table 3.

TABLE 3

MOLECULAR REFRACTION (R_M) DATA FOR ORGANOTIN AND ORGANOSILICON COMPOUNDS

Compound	R_M (calculated)		R_M (observed)	Difference (%)	
	R–N=C=S	R–S–C≡N		R–N=C=S	R–S–C≡N
Tributyltin (iso)thiocyanate	89·09	87·13	88·86	+0·2	−2·0
Triethyltin (iso)thiocyanate*	61·20	59·24	60·49	+1·2	−2·1
Trimethylsilicon (iso)thiocyanate	40·47	38·21	40·18	+0·7	−4·7
Dimethylsilicon di-(iso)thiocyanate	50·76	46·24	49·92	+1·7	−7·4

* Lit.[5] n_D^{20} 1·5825, d_4^{20} 1·4580.

On the basis of refraction data calculated from atomic refractions, Anderson[21] concluded that a series of methyl silicon (iso)thiocyanates exist mainly as isothiocyanates. Recalculation of molecular refractions from bond refraction data has confirmed this observation, and the results of these calculations are given in Table 3. These calculations indicate that both trialkyltin (iso)thiocyanates and alkyl silicon (iso)thiocyanates exist mainly as isothiocyanates.

TRIBUTYLTIN ISOCYANIDE

(a) *Chemical Data*

Seyferth and Kahlen[6] have prepared trimethyltin (iso)thiocyanate by the reaction of trimethyltin (iso)cyanide and sulphur at 150–160°. We have shown that

[19] Vogel, A. I., Cresswell, W. T., Jeffrey, G. H., and Leicester, J., *J. Chem. Soc.*, 1952, 514.
[20] Vogel, A. I., Cresswell, W. T., Leicester, J., *J. Phys. Chem.*, 1954, **58**, 174.
[21] Anderson, H. H., *J. Amer. Chem. Soc.*, 1947, **69**, 3049.

tributyltin (iso)cyanide will react with sulphur under the same conditions, or in boiling carbon disulphide solution, to form tributyltin isothiocyanate; the infrared spectra of the crude and the redistilled products being identical. Since isomerization is unlikely at 46° it appears reasonable that the starting material may be mainly the isocyanide.

Van der Kerk and his colleagues[10,22] have surveyed the reactions for the formation of tin–carbon bonds, and shown that, in general, these bonds may be formed by Grignard, Wurtz, disproportionation, or decarboxylation reactions and showed that tributyltin chloride and potassium cyanide react in cold alcohol. Under these conditions, it is unlikely that a tin–carbon bond would be readily formed but more probable that the bond is between tin and nitrogen.

(*b*) *Infrared and Molecular Refraction Data*

The infrared spectrum of tributyltin (iso)cyanide is given in Figure 1, and intensity data on the (iso)cyanide band in Table 2. Integrated absorption intensity measurements do not provide as definite a difference between the two (iso)cyanide isomers as with the (iso)thiocyanates because of the weakness of the infrared absorption. Ugi and Meyer[23] in a series of measurements on several organic isocyanides give a range of values, all above 0·3 units. Mander and Thompson,[24] Brown,[25] and Bayliss, Cole, and Little[26] give a range of values from 0·042 for acetonitrile to 0·82 for *p*-aminobenzonitrile with, in general, alkyl cyanides giving values below 0·1. It is clear that the intensity of the C≡N absorption is markedly dependent on its immediate atomic environment and that although the value of 0·076 obtained for tributyltin (iso)cyanide lies within the cyanide range and below that of the isocyanides, the assignment to cyanide is very tentative, particularly in the light of the chemical evidence discussed above.

The refractive index of solid tributyltin (iso)cyanide can be determined by application of the law of mixtures as described by Partington,[27] and the molecular refraction calculated. According to Gillis,[28] (N=C) is 5·17 and (C=N) is 4·82, and hence (Sn–N=C) is 9·19 and (Sn–C=N) is 8·98. The difference between these values is within the limits of experimental error for the determination of refractive index by the solution technique, and thus refraction data cannot be used to distinguish between these two compounds.

Although infrared and molecular refraction data are inconclusive, chemical evidence indicates that the compound may exist as tributyltin isocyanide, but further experimental evidence seems desirable.

[22] Van der Kerk, G. J. M., and Noltes, J. C., *J. Appl. Chem.*, 1959, **9**, 113.
[23] Ugi, I., and Meyer, R., *Chem. Ber.*, 1960, **93**, 239.
[24] Mander, M. R., and Thompson, H. W., *Trans. Faraday Soc.*, 1957, **53**, 1402.
[25] Brown, T. L., *J. Amer. Chem. Soc.*, 1958, **80**, 794.
[26] Bayliss, N. S., Cole, A. R. H., and Little, L. H., *Spectrochim. Acta*, 1958, **1**, 12.
[27] Partington, J. R., "An Advanced Treatise on Physical Chemistry." Vol. IV, p. 72. (Longmans: London 1953.)
[28] Gillis, R. G., *J. Org. Chem.*, 1962, **27**, 4103.

Experimental

Infrared spectra were measured on a Perkin–Elmer Model 125 spectrophotometer. The frequencies are accurate to within 2 cm^{-1} for the isothiocyanate and 1 cm^{-1} for the (iso)cyanide. The intensity measurements were performed in pure dry solvents using a spectral slit width of 1·5 cm^{-1}. The areas were measured by planimeter and no wing corrections were applied. The unit of intensity used is 10^4 $mole^{-1}$ litre cm^{-2}.

Tin determinations were carried out using the method of Luijten and van der Kerk.[10] Samples were oxidized by Parr bomb combustion and sulphur was determined gravimetrically. Nitrogen was determined volumetrically after Kjeldahl digestion.

Starting Materials.—Tributyltin oxide was refractionated commercial material with b.p. 180°/1·0 mm, n_D^{20} 1·4868. Treatment of tributyltin oxide with thionyl chloride followed by degassing and refractionation gave tributyltin chloride with b.p. 146°/4·0 mm, n_D^{20} 1·4922.

Tributyltin (iso)cyanide was prepared by the method of Luijten and van der Kerk[9] and purified by distillation at 132–134°/0·5 mm followed by sublimation at 1·0 mm. It had m.p. 91°.

Tributyltin sulphide, prepared by the method of Chauny and Cirey[29] using 95% ethanol as the solvent, had b.p. 172°/0·2 mm, n_D^{20} 1·5180, d_4^{20} 1·1930, R_M 155·4. The yield was 72%.

Reactions of Thiourea Compounds with Tributyltin Compounds.—The reactions of tributyltin oxide and tributyltin chloride with thiourea and *NN'*-disubstituted thioureas are set out in Table 1. The experimental procedure for the reaction between thiourea and tributyltin oxide (Table 1, reaction 2) is typical for the reactions described.

Tributyltin oxide (119·2 g; 0·2 mole) was placed in a three-necked flask fitted with a stirrer, gas inlet, and gas outlet leading to a bubbler containing saturated boric acid. Anhydrous powdered thiourea (15·2 g; 0·2 mole) was added and dry nitrogen bubbled through the stirred mixture, while the temperature was maintained at 200° for 8 hr. The ammonia liberated was estimated by titration and, after cooling, ether (250 ml) was added to the reaction mixture, and any insoluble material filtered off. The ether was removed under vacuum and the product distilled through a 15-in. Vigreux column to give *tributyltin isothiocyanate*, b.p. 160–162°/0·8 mm, n_D^{20} 1·5417, in a yield of 15% (Found: N, 4·0; S, 9·1; Sn, 34·0%. Calc. for $C_{13}H_{27}NSSn$: N, 4·0; S, 9·2; Sn, 34·1%). Tributyltin sulphide, b.p. 175°/0·5 mm, n_D^{20} 1·5176, was also formed in a yield of 70% (Found: S, 5·3; Sn, 38·5%. Calc. for $C_{24}H_{54}SSn_2$: S, 5·2; Sn, 38·8%).

In the reaction between tributyltin oxide and *NN'*-diphenylthiourea (Table 1, reaction 3) the reactants were refluxed in toluene for 8 hr. After cooling *NN'*-diphenylurea, m.p. 242°, was removed by filtration and the product, tributyltin sulphide, n_D^{20} 1·5178, recovered by fractionation.

In the reactions between *NN'*-diethylthiourea (Table 1, reaction 4) and *NN'*-dibutylthiourea (Table 1, reaction 5) with tributyltin oxide, stirring was carried out for 5 hr. Light petroleum was then added, insoluble material removed, and tributyltin sulphide was recovered by fractionation. The by-products *NN'*-diethylurea, m.p. 107°, and *NN'*-dibutylurea, m.p. 68°, were purified by recrystallization from isooctane and identified by their infrared spectra.

Tributyltin isothiocyanate was also obtained by the reaction of tributyltin chloride, (65·2 g; 0·2 mole) with powdered thiourea, (16·5 g; 0·22 mole) at 170° for 12 hr (Table 1, 1). The fractionated product had b.p. 160°/0·5 mm, n_D^{20} 1·5382, and was obtained in a yield of 16%. Tributyltin chloride, n_D^{20} 1·4892, was recovered unchanged in a yield of 59%.

Reactions of Inorganic Thiocyanates with Tributyltin Compounds.—Tributyltin chloride (65·2 g; 0·2 mole) was dissolved in 200 ml of 95% ethanol and treated with a solution of potassium thiocyanate (24·3 g in 50 ml of the same solvent). After heating under reflux for 2 hr the solution was cooled and the precipitated potassium chloride removed by filtration. Alcohol was removed under vacuum and the residue dissolved in 200 ml of ether, washed twice with water, and dried. Fractionation gave tributyltin isothiocyanate, b.p. 146°/0·2 mm, n_D^{20} 1·5432, d_4^{20} 1·2350, R_M 88·86, in a yield of 91% (Found: N, 4·0; S, 9·0; Sn, 33·6%).

[29] Chauny, A., and Cirey, L. V., Brit. Pat. 792,309. (*Chem. Abstr.*, 1958, **52**, 17805.)

The reaction between tributyltin oxide and potassium thiocyanate was carried out at 80° on a 0·1 mole scale using 100 ml of 2N hydrochloric acid as the reaction medium. After the reaction was complete (0·5 hr) ether (200 ml) was added and tributyltin isothiocyanate was recovered in a yield of 66% from the dried ether layer by fractionation.

In the reaction between tributyltin chloride (65·2 g; 0·2 mole) and anhydrous silver thiocyanate (41·5 g; 0·25 mole), the reactants were heated on an oil-bath at 180° for 4 hr. After cooling, light petroleum (200 ml) was added, the insoluble matter removed, and the product, tributyltin isothiocyanate, was recovered in a yield of 15% by fractionation. It had n_D^{20} 1·5417 (Found: N, 4·0; S, 9·1; Sn, 34·0%).

The reaction between tributyltin chloride and ammonium thiocyanate was carried out using the same conditions as used with the potassium thiocyanate reaction described above. The fractionated tributyltin isothiocyanate had b.p. 152–154°/0·4 mm, n_D^{20} 1·5434, and the yield was 50% (Found: N, 4·0; S, 9·2; Sn, 34·0%).

After heating tributyltin isothiocyanate under vacuum (180° at 0·3 mm) for 3 hr no change was observed in the refractive index, the boiling point, and the infrared spectrum of a redistilled sample.

Reactions of Tributyltin (Iso)cyanide.—Tributyltin (iso)cyanide (31·6 g; 0·1 mole) and sulphur (3·2 g; 0·1 mole) were dissolved in carbon disulphide (200 ml) and refluxed on a water bath for 8 hr. While the temperature was kept below 45° the solvent was removed under vacuum to give a crude product with n_D^{20} 1·5398. Refractionation gave tributyltin isothiocyanate, b.p. 150–152°/0·4 mm, n_D^{20} 1·5428, in a yield of 80%.

Sulphur (1·6 g; 0·05 mole) and tributyltin (iso)cyanide (15·8 g; 0·05 mole) were heated under nitrogen at 160° for 4 hr. The liquid slowly darkened, and on cooling had n_D^{20} 1·5380. Distillation gave tributyltin isothiocyanate, b.p. 150–154°/0·4 mm, n_D^{20} 1·5402, in a yield of 62% (Found: N, 4·0; Sn, 34·1%).

Tributyltin Succinimide.—Tributyltin oxide (59·6 g; 0·1 mole) and succinimide (19·8 g; 0·2 mole) were heated together for 2 hr at 160°. The water liberated was removed under vacuum and the product distilled (b.p. 144°/0·2 mm). The yield was 79%, and the product had n_D^{20} 1·5086, d_4^{20} 1·230, m.p. 21°, R_M 94·16 (Found: Sn, 30·4; N, 3·6%. Calc. for $C_{16}H_{31}NO_2Sn$: Sn, 30·6; N, 3·6%).

Acknowledgment

Thanks are due to Mr. D. J. Boyd for the analytical data. This communication is published by permission of the Chief Scientist, Department of Supply, Australian Defence Scientific Service, Melbourne.

APPENDIX 10 INFRARED STUDIES ON ORGANOTIN COMPOUNDS

10f Some Reactions of Organotin Azides
P. DUNN and D. OLDFIELD
Aust. J. Chem., 24, No. 3, 645-7 (1971) 10.66 - 10.69

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AUSTRALIAN JOURNAL OF CHEMISTRY

SOME REACTIONS OF ORGANOTIN AZIDES

By P. DUNN* and D. OLDFIELD*

[Manuscript received October 12, 1970]

We are prompted by recent interest in the chemistry of organometallic azides of Group IV elements[1,2] to report the results of some addition reactions of organotin azides.

Aminostannylation of unsaturated substrates occurs readily[3]

$$Me_3SnNMe_2 + A{=}B \rightarrow Me_3Sn{-}A{-}B{-}NMe_2$$

so that it was of interest to see if tributyltin azide would undergo similar reactions.

Reaction with –N=C=S

Tri-n-butyltin azide, a stable, distillable liquid, reacted readily at room temperature with phenyl isothiocyanate to give a crystalline product analysing correctly for a 1 : 1 adduct to which we have assigned structure (1). Treatment of this compound with cold dilute hydrochloric acid produced 1-phenyltetrazole-5-thiol (2)[4] and tributyltin chloride, whilst treatment with cold aqueous sodium hydroxide produced (2) and bis(tributyltin) oxide.

Phenyl isothiocyanate is reported[4] to react with hydrazoic acid to give initially 5-phenylamino-1,2,3,4-thiatriazole (3) which is converted into (2) by base. A small amount of (3) was obtained in the reaction of crude tributyltin azide with phenyl isothiocyanate, but none was found when using the distilled azide. It was found that (3) was not converted into (2) by the acidic conditions employed in our hydrolysis. This means that the present hydrolysis conditions do not alter the structure of the ring system so that the adduct (1) must contain the tetrazole ring as postulated. Cleavage of the tin–nitrogen bond then leads to the observed products in both cases. The ultraviolet spectra of authentic specimens of (2) and (3) were found particularly useful in confirming that it was in fact (2) which has been isolated in both hydrolyses. The ultraviolet absorption of (1) (λ_{max} 265 nm) is closer to that of (2) (λ_{max} 276 nm) than to that of (3) (λ_{max} 302 nm).

Triphenyltin azide reacted smoothly at 140° with phenyl isothiocyanate to give the analogous adduct (4) which was cleaved by dilute hydrochloric acid to (2).

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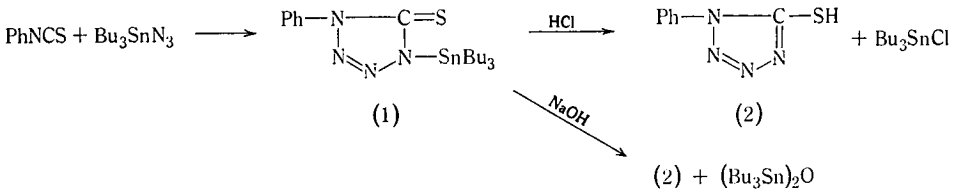
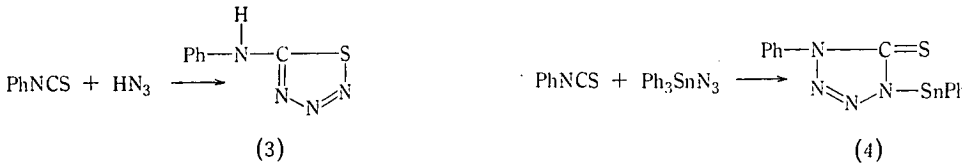
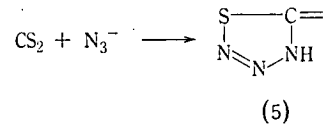
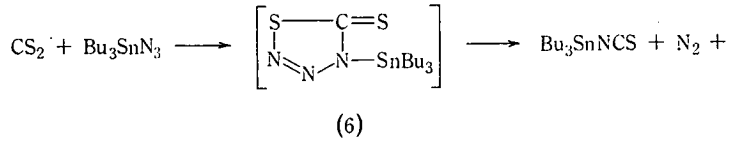
[1] Tsai, T.-T., Lehn, W. L., and Marshall, C. J., *J. organomet. Chem.*, 1970, **22**, 387.
[2] Wiberg, N., and Joo, W. C., *J. organomet. Chem.*, 1970, **22**, 333.
[3] George, T. A., Jones, K., and Lappert, M. F., *J. chem. Soc.*, 1965, 2157.
[4] Lieber, E., and Ramachandran, J., *Can. J. Chem.*, 1959, **37**, 101.

Diphenylurea was the only product isolated from the reaction of tributyltin azide with phenyl isocyanate even when precautions were taken to exclude moisture.









Reaction with S=C=S

Reaction of carbon disulphide with azide ion gives[5] the cyclic thiatriazoline-thione (5) which absorbs in the ultraviolet at 313 nm and decomposes above 10°.

Tributyltin azide has been found by other workers[6] to react with carbon disulphide in boiling diethyl ether to give tributyltin isothiocyanate and sulphur.

In the present work tributyltin azide was added to an excess of carbon disulphide at room temperature and the ultraviolet spectra of aliquots of the mixture dissolved in methanol were examined at regular intervals. A new strong absorption maximum near 285 nm appeared after 19 hr. The reaction mixture decomposed to tributyltin isothiocyanate, identified by its i.r. and u.v. spectra,[7] when the carbon disulphide was allowed to evaporate at room temperature. Heating the reaction mixture on a steam-bath for only 5 min also produced the same decomposition reaction, with evolution of

[5] Lieber, E., Oftedahl, E., and Rao, C. N. R., *J. org. Chem.*, 1963, **28**, 194.

[6] Luijten, J. G. A., personal communication.

[7] Cummins, R. A., and Dunn, P., *Aust. J. Chem.*, 1964, **17**, 411.

gas. We believe that the spectroscopic evidence supports the reaction mechanism outlined, which proceeds via the intermediate (6). No reaction was observed between tributyltin azide and carbon dioxide.

Experimental

Tri-n-butyltin azide and triphenyltin azide were prepared by the reported procedures.[8] Microanalyses were performed by Australian Microanalytical Service, Melbourne.

1-Phenyl-4-(tributylstannyl)tetrazole-5-thione (1)

Tributyltin azide (2·0 g; 6 mmol) was added to phenyl isothiocyanate (0·7 ml; 6 mmol) and the mixture was allowed to stand at room temperature for 24 hr. The solid product was crystallized from hexane as colourless plates of *1-phenyl-4-(tributylstannyl)tetrazole-5-thione* (2·13 g; 4·5 mmol), m.p. 45–48° (Found: C, 49·5; H, 6·9; N, 12·1; S, 6·6. $C_{19}H_{32}N_4SSn$ requires C, 48·8; H, 6·8; N, 12·0; S, 6·9%).

Hydrolysis by Hydrochloric Acid

1-Phenyl-4-(tributylstannyl)tetrazole-5-thione (1·0 g; 2 mmol) in ether (50 ml) was stirred with 4N hydrochloric acid (30 ml) at room temperature for 8 hr. Ether (100 ml) was then added, the organic layer was separated, washed with water (2 × 150 ml), and dried ($MgSO_4$), and the ether was distilled to leave a mixture of a white solid and a yellow liquid. The mixture was filtered; the filtrate (0·38 g; 1 mmol) had the correct i.r. spectrum for tributyltin chloride. After rinsing with a little hexane, the white solid (0·2 g; 1 mmol), m.p. 145–150°, was shown to have the same u.v. spectrum as an authentic sample of 1-phenyltetrazole-5-thiol (lit.[4] m.p. 147–150°), and with mixed melting point undepressed.

Hydrolysis by Sodium Hydroxide

1-Phenyl-4-(tributylstannyl)tetrazole-5-thione (1·0 g; 2 mmol) was stirred with sodium hydroxide (1·5 g) in water (30 ml) at 18° for 6 hr. The resulting clear solution was extracted with ether (2 × 150 ml), the aqueous layer was acidified with 4N hydrochloric acid and the white precipitate formed was filtered and crystallized from ethanol as 1-phenyltetrazole-5-thiol (0·25 g; 1·4 mmol), m.p. 145–150°, with the correct u.v. spectrum. The ether extracts were combined, dried ($MgSO_4$), and the ether distilled to leave a colourless liquid (0·99 g; 1·6 mmol) identified by its i.r. spectrum as bis(tributyltin) oxide.

1-Phenyl-4-(triphenylstannyl)tetrazole-5-thione

Triphenyltin azide (1·0 g; 2·5 mmol) and phenyl isothiocyanate (0·3 ml; 2·5 mmol) was stirred together at 140° for 3 hr. The brown residue was extracted with boiling hexane and on cooling the extract gave white crystals of *1-phenyl-4-(triphenylstannyl)tetrazole-5-thione* (0·3 g; 0·6 mmol), m.p. 129–137° (Found: C, 57·1; H, 3·8; N, 10·8; S, 6·1. $C_{25}H_{20}N_4SSn$ requires C, 56·9; H, 3·8; N, 10·6; S, 6·1%).

Hydrolysis by Hydrochloric Acid

1-Phenyl-4-(triphenylstannyl)tetrazole-5-thione (0·096 g) in ether (50 ml) was stirred with 4N hydrochloric acid (30 ml) at room temperature for 6 hr. The ether layer was separated, washed with water (200 ml), dried ($MgSO_4$), and the ether distilled to leave a light green solid (0·09 g) whose u.v. spectrum showed it to contain 1-phenyltetrazole-5-thiol.

[8] Luijten, J. G. A., Janssen, M. J., and van der Kerk, G. J. M., *Recl Trav. chim. Pays-Bas*, 1962, **81**, 202.

APPENDIX 11 ORGANOTIN FLUORIDES

11a Tri-n-butyltin Fluoride - A Novel Coordination Polymer in Solution.
P. DUNN and D. OLDFIELD
J. Macromol. Sci. - Chem., A4 (5), 1157-1168 (1970) 11.2 - 11.13

11b The Formation of Tri-n-butyltin Fluoride from Tetrafluoro-hydroquinone.
P. DUNN and D. OLDFIELD
J. Organometal. Chem., 23, 459-60 (1970). 11.14 - 11.15

11c Some Reactions of Organotin Compounds Under γ-irradiation.
P. DUNN and D. OLDFIELD
J. Organometal. Chem., 54, C11-C12 (1973). 11.16 - 11.17

. MACROMOL. SCI.–CHEM., A4(5), pp. 1157-1168, August, 1970

Tri-n-butyltin Fluoride. A Novel Coordination Polymer in Solution

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Department of Supply
Island Vale, Victoria, 3032, Australia

SUMMARY

Tri-n-butyltin fluoride dissolves in nonpolar organic solvents to give viscous solutions which are believed to contain polymeric aggregates of the organotin compound. Certain organic compounds when added to these viscous solutions can cause marked changes in viscosity. These changes have been studied to gain an insight into the structure of the aggregates.

INTRODUCTION

It is now generally accepted that in the solid state tin(IV) may form five-coordinate complexes when bound to suitable ligands. Much of this work has recently been reviewed by Davies [1] while Janssen and others [2] showed that tri-n-butyltin imidazole exists as a linear polymeric chain in solution, in toluene, as well as in the crystalline state.

The structure of crystalline trimethyltin fluoride has been shown [3] in an x-ray study, to consist of a polymeric chain of penta-coordinate tin atoms, linked by bridging fluorine atoms. Several inorganic compounds, such as molybdenum oxyfluoride [4] and rhenium oxyfluoride [5] have recently been shown to have crystal structures involving bridging fluorine atoms.

The present study resulted from the observation that tri-n-butyltin

fluoride, although insoluble in most organic solvents, would dissolve in som to give very viscous solutions. The work presented is believed to be the first evidence for the existence of bridging fluorine atoms in solution and is provided by nonspectroscopic means, in contrast to most recent studies on similar systems.

The work is presented in the same way as the earlier paper by Janssen and others [2] to enable a comparison to be made between the two systems. In the first section, a model for the structure of solutions of tri-n-butyltin fluoride is presented which rationalizes all the results obtained in this study. The second section deals with the effect of a wide variety of additives on the viscosity of solutions of tri-n-butyltin fluoride in an effort to elucidate the type of bonding occurring in these solutions.

EXPERIMENTAL

Tri-n-butyltin fluoride was prepared by the reaction of ammonium fluoride on bis(tri-n-butyltin) oxide as previously reported [6] crystallized from methanol, and carefully dried before use. All solvents were fractionated. Viscosity determinations were made at 37° in a suspended level viscometer incorporating a sintered-glass filter disk [7]. This temperature was chosen as being near to 100°F (37.7°C) used in much standard viscometric work, and was found to be a suitable compromise between the higher viscosities on the one hand or solvent evaporation on the other encountered at lower and higher temperatures, respectively.

The kinematic viscosity (ν) was calculated from the usual equation:

$$\nu = \frac{\eta}{\rho} = At - \frac{B}{t}$$

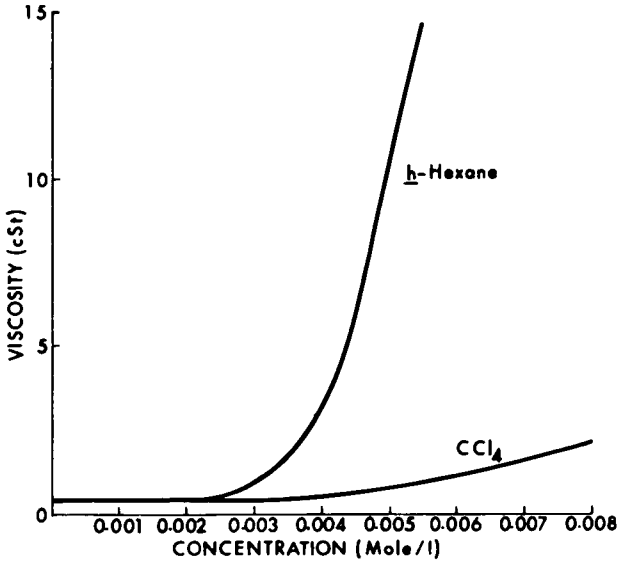
where the constants A and B were determined from measurements on liquids of known viscosity, and t was the measured time of flow. The viscosity is expressed throughout in centistokes (cSt).

The effect of certain additives on solution viscosity was investigated by shaking measured amounts of the additive in stoppered tubes with 10 ml of a solution (2 g/liter, 0.0064 mole/liter) of tri-n-butyltin fluoride in n-hexane. Solution viscosity was measured at 37° and a graph plotted of solution viscosity vs additive concentration.

RESULTS AND DISCUSSION

Tri-n-butyltin Fluoride Solutions

Tri-n-butyltin fluoride is insoluble in many organic solvents, but dis-
ves to the extent of about 2% in methanol to give nonviscous solutions.
contrast, it dissolves slowly to the same extent in carbon tetrachloride
in n-hexane to give very viscous solutions. The increase in viscosity
h concentration for these two solvents is shown in Fig. 1.



. 1. Effect of concentration on the viscosity of solutions of tri-n-butyltin fluoride in n-hexane and carbon tetrachloride at 37°.

High molecular weight compounds dissolve in organic solvents to produce
ous solutions, and the viscosity increase of the solution over that of the
vent can be related to the molecular weight of the solute. This effect
ally becomes apparent when the molecular weight of the solute is above
eral thousand [8]. We believe that the viscosity increase observed with
utions of tri-n-butyltin fluoride is due to the presence of polymeric ag-
gates of the compound in the solution. However, the increase in viscosity
h concentration was so rapid that no reliable estimate of the molecular
ght could be made from the solution viscosity.

The viscous solutions appear to be produced by swelling and dissoluti of the organotin compound over the course of a few days. The increase in viscosity of the solution becomes apparent at a solute concentration c only 0.003 mole/liter, suggesting that even in very dilute solution the or- ganotin fluoride is present as polymeric chains of sufficient length to sig- nificantly increase the viscosity of the solvent. Table 1 lists the properti of some solutions of tri-n-butyltin fluoride, of tri-n-butyltin imidazole an for comparison, of polystyrene. The efficiency of tri-n-butyltin fluoride producing these viscous solutions, as compared to that of tri-n-butyltin imidazole or of polystyrene, is evident.

The behavior of the organotin compound in solution can be explained by considering that a single isolated tri-n-butyltin fluoride molecule will possess a dipole moment due to the electronegativity difference between tin and fluorine. This could lead to a weak dipole-dipole type interactio between adjacent molecules, resulting in the tin atoms becoming penta- coordinate and linked through fluorine bridges in the type of structure already reported [3] for crystalline compounds such as trimethyltin fluoride. As all the organotin molecules in solution possess this dipole moment, an infinitely long, linear, polymer chain could be formed.

Solid tri-n-butyltin fluoride might be considered as being analogous to a two-dimensional ionic crystal lattice, but with dipole-dipole rather than ionic forces holding the molecules together in the solid state. Sol- vent molecules of a suitable molecular size and zero dipole moment will slowly permeate the solid to produce a viscous solution by a slow swell- ing process as is observed in practice. Solvents which do this are carbon tetrachloride and n-hexane. Other alkanes will not dissolve the com- pound. The structure is represented diagrammatically in Fig. 2.

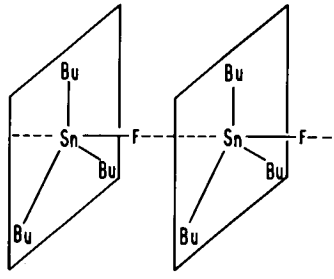


Fig. 2. Diagrammatic representation of long chains of tri-n-butyltin fluoride in nonpolar solvents.

Table 1. Solution Properties of Some Organotin Compounds and of Polystyrene at 37°

Compound	Solvent	Solvent dipole moment (D) [9]	Solvent viscosity (cSt)	Solution viscosity[a] (cSt)
Tri-n-butyltin fluoride	n-Hexane	0	0.4	300
	Carbon tetrachloride	0	0.5	200
	Tetrachloroethylene	0	0.5	190
	Trichloroethylene	0.8	0.3	0.7
	Chloroform	1.0	0.3	0.3
	1, 1, 1-Trichlorethane	1.8	0.5	2.8
Tri-n-butyltin imidazole	n-Hexane	0	0.4	2.4
Polystyrene	Toluene	–	0.6[b]	1.0

[a]Concentration of all solutions, 10 g/liter.
[b]At 30°.

The molecular size of chloroform is similar to that of carbon tetrachlo ide, and it can also penetrate solid tri-n-butyltin fluoride to form a soluti Because it has a dipole moment it interacts with the organotin molecules give monomers with the tin atom coordinated to the solvent rather than another tri-n-butyltin fluoride molecule. The polymeric nature of the so is thus destroyed, and the viscosity of the solution is similar to that of tl pure solvent.

An intermediate form of interaction producing solvated oligomers wou lead to a partial reduction in the solution viscosity. This situation exists with tetrachloroethylene and with trichloroethylene (Table 1). The form compound, which has no dipole moment, gives viscous solutions with tri n-butyltin fluoride, indicating that it has a suitable molecular size, where trichloroethylene with a similar size, but having a dipole moment, gives a nonviscous solution with the same concentration of organotin compound

Thus polar solvents can compete successfully with the organotin molecules for the fifth coordination position of the tin atom, as is shown in Fig. 3.

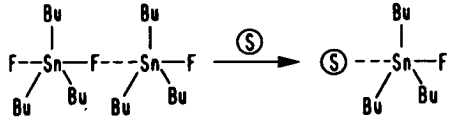


Fig. 3. Diagrammatic representation of the effect of polar solvents on th properties of tri-n-butyltin fluoride molecules in solution.

The behavior of tri-n-butyltin fluoride both in the solid and in viscous and nonviscous solutions is consistent with the reversible nature of the type of interaction suggested. It also illustrates the weakness of the bon ing, whether to solvent molecules or to other molecules of tri-n-butyltin fluoride. The relative insolubility of the fluoride in most organic solvent is probably due to the inability of these solvents to penetrate the crystal lattice.

Although several instances have been reported where fluorine acts as a bridging atom in organometallic or inorganic compounds in the solid, this is the first time such an effect has been noted in solution. An x-ray diffraction study of tri-n-butyltin fluoride in the solid state, and as a viscous solution in carbon tetrachloride, has confirmed the same general polymeric structure in both states.

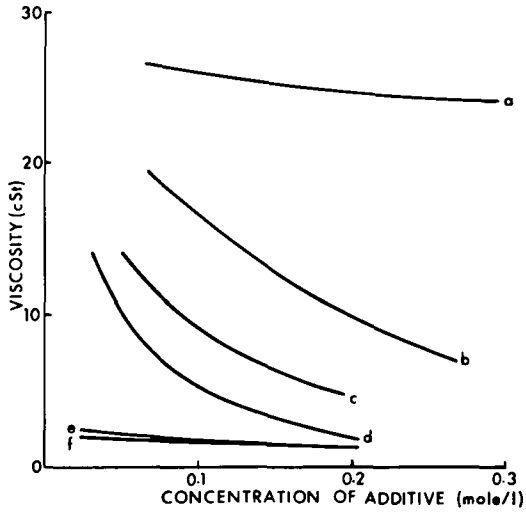
The interaction of organotin fluoride molecules in solution, being only

ctrostatic in nature, can be easily disrupted by the addition of certain npounds, and this effect has been further investigated.

Effect of Additives on Solution Viscosity

When small amounts of certain compounds are added to viscous solutions tri-n-butyltin fluoride in n-hexane (0.2%, w/v solution), a marked reduction the viscosity of the solution can occur. By comparing the reduction in cosity of solutions at the same molar concentration of additive, an indica- n of the relative complexing ability of the additive can be obtained. mplexing may take the form of the dipolar solvation noted with the ogenated solvents or the form of a specific interaction between the ad- ive and the tin atom to give a new penta-coordinate species. Previous rk [1, 6] has shown that trialkyltin halides form stable 1:1 complexes h nitrogen bases, and these complexes can, under favorable conditions, be lated. This is the type of interaction expected to occur with tri-n-butyltin oride.

The effect of adding various compounds to viscous solutions of tri-n- tyltin fluoride in n-hexane is shown in Fig. 4. For subsequent comparisons, viscosities of the solutions in the presence of 0.1 mole/liter of additive



g. 4. Graph showing the effect of various additives on a solution (0.2% v) of tri-n-butyltin fluoride in n-hexane at 37°. The additives are: (a) uene, (b) chloroform, (c) acetophenone, (d) methanol, (e) triethylamine, and (f) N,N-dimethyl-formamide.

were determined from graphs plotted for each additive. The viscosities o the solution without additives and of the pure solvent were 27 and 0.4 c respectively.

The nitrogen-containing bases are the most effective of the additives studied in reducing the solution viscosity to that of the pure solvent. Th implies that these compounds coordinate most strongly with the organoti fluoride. By comparison, other compounds such as toluene interact only very weakly with the organotin compound in solution, if at all. As the solution contains 0.0064 mole/liter of organotin fluoride, there is about a sixteenfold molar excess of the additive when used at a concentration of 0.1 mole/liter. The most effective additives, however, reduced the soluti viscosity to that of the solvent at concentrations much below this, and ir the case of piperidine the concentration was 0.03 mole/liter, or roughly a fivefold excess.

The effect of a range of nitrogen-containing additives on the solution viscosity of tri-n-butyltin fluoride in n-hexane is given in Table 2.

Table 2. Effect of Amine-Type Additives on Solutions of Tri-n-butyltin Fluoride in n-Hexane

Additive[a]	Solution viscosity (cSt)[b]
Solvent, n-hexane	0.4
Solution, no additive	27.0
N,N-Diethylaniline	19.5
Aniline	6.2
Triethylamine	1.0
Diethylamine	0.6
1,2-Diaminopropane	0.5
Dimethyl formamide	0.5
N-Ethyl formamide	0.4
Piperidine	0.4

[a]Concentration of additive, 0.1 mole/liter.

[b]Concentration of tri-n-butyltin fluoride, 2 g/liter 0.0064. mole/liter, at 37°.

All the additives capable of reducing the solution viscosity to less than
:St are, within experimental error, considered to be equally effective. Sub-
tution on the nitrogen atom in the additives by alkyl groups has little
ect on the complexing ability of the compound, and this suggests that
basicity of the nitrogen is the determining factor. In aniline and
thylaniline the aromatic ring could be reducing this basicity by electron
hdrawal from the nitrogen towards the aromatic ring. Amines and
ides appear to be of comparable effectiveness, indicating that the extent
coordination of tri-n-butyltin fluoride with both these types of additives
similar.

The incorporation of the nitrogen into a heterocyclic ring system also
ects the activity of the additive and the results for four such compounds
given in Table 3(A).

Pyridine is a weaker ligand than its saturated analog piperidine, whereas
rrole occupies an intermediate position between these compounds. A
mparison of the activity of pyrrole with that of furan and thiophene is
own in Table 3(B). Likewise a comparison of pyrrole with pyrrolidine
d furan with tetrahydrofuran also shows that the saturated analog has
e greater complexing ability. As shown in Table 3(C), amides are more
fective complexing agents for tri-n-butyltin fluoride than ketones.

The effect of a number of halogenated compounds in reducing the vis-
sity of solutions of tri-n-butyltin fluoride in n-hexane has also been
vestigated. The results are given in Table 4, together with some reported
ues for dipole moments.

Additives with a large dipole moment interact with the organotin fluoride
reduce the viscosity of the solutions, whereas additives with no dipole
oment, such as carbon tetrachloride and tetrachloroethylene, have little
no effect.

Within a particular series of additives an approximate correlation exists
tween the dipole moment and the extent to which the solution viscosity
reduced by the additive, that is, the extent to which the polymeric chains
e disrupted. Carbon tetrachloride, with no dipole moment, has negligible
fect, fluorotrichloromethane (dipole moment, 0.45 D) reduces the vis-
sity to 25 cSt, while chloroform (dipole moment, 1.02 D) reduces the
cosity even further to a value of 14 cSt.

Replacing a given atom in an additive by one of greater atomic weight
es compounds with greater effectiveness in reducing the viscosity of
ganotin fluoride solutions. Thus deuterochloroform is more effective
an chloroform, and tetrabromoethane is more effective than tetra-
loroethane.

Table 3. Effect of Additives on Solutions of Tri-n-butyltin Fluoride in n-Hexane

A		B		C	
Additive[a]	Solution[b] viscosity (cSt)	Additive[a]	Solution[b] viscosity (cSt)	Additive[a]	Solution[b] viscosity (cSt)
Aniline	6.2	Furan	24.0	Acetone	9.3
Pyridine	2.3	Thiophene	21.0	Acetophenone	7.8
Pyrrole	1.4	Tetrahydrofuran	8.4	N,N-Dimethylformamide	0.8
		Pyrrole	1.4		
Piperidine	0.5	Pyrrolidine	0.4	N-Ethylformamide	0.5

[a]Concentration of additive, 0.1 mole/liter.
[b]Concentration of tri-n-butyltin fluoride, 2 g/liter, 0.0064 mole/liter, at 37°.

ble 4. Effect of Halogenated Compounds on Solutions of Tri-n-butyltin Fluoride in n-Hexane

Additive[a]	Dipole moment [9] of additive (D)	Solution[b] viscosity (cSt)
rbon tetrachloride	0	27
uorotrichloromethane	0.45	25
loroform	1.02	14
euterochloroform	[c]	12
trachloroethylene	0	27
ichloroethylene	0.8	24
n-Tetrachloroethane	1.3	9
n-Tetrabromoethane	1.7	7
1,1-Trichloroethane	1.8	22
Chlorobutane	2.1	22

[a]Concentration of additive, 0.1 mole/liter.
[b]Concentration of tri-n-butyltin fluoride, 2 g/liter, 0.0064 mole/liter, at °.
[c]Not available.

The effects noted earlier (Section A) of the polar halogenated solvents solution viscosity appear to be the same as when these same compounds e used as additives to reduce the viscosity of solutions of tri-n-butyltin oride in n-hexane. This suggests that the n-hexane fits into the spaces ound the polymeric chain in the solid without disrupting the dipole-dipole rces that cause aggregates of the organotin fluoride to form. The addi- n of polar solvents to the viscous solutions disrupts the forces holding e polymeric chains together, thus splitting the chains, and this results in reduction in solution viscosity.

The greater activity of the nitrogen-containing bases, especially those th an unhindered nitrogen atom, indicates a specific interaction in this se between the lone pair and the tin atom. The polymeric tri-n-butyltin oride in solution is broken down to a type of complexed monomer, com- sing a penta-coordinated tin atom bonded to a molecule of the base, ree n-butyl groups, and a fluorine atom.

The effect of additives on the solution properties of tri-n-butyltin fluo dissolved in n-hexane supports the proposed polymeric structure of the co pound in solution.

ACKNOWLEDGMENT

The assistance of Dr. D. A. Wright of Defence Standards Laboratories performing the x-ray analysis is acknowledged.

REFERENCES

[1] A. G. Davies, *Chem. Brit.*, 4, 403 (1968).
[2] M. J. Janssen, J. G. A. Luijten, and G. J. M. Van der Kerk, *J. Orga metal. Chem.*, 1, 286 (1964).
[3] H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, **1964**, 23
[4] A. J. Edwards and B. R. Steventon, *J. Chem. Soc., A*, **1968**, 2503.
[5] A. J. Edwards and G. R. Jones, *J. Chem. Soc., A*, **1968**, 2511.
[6] P. Dunn and T. Norris, *The Preparation of Organotin Compounds,* Report No. 269, Defence Standards Laboratories, Department of Supply, Australia, 1964, p. 13.
[7] G. W. Harding, *J. Polym. Sci.*, 55, S27 (1961).
[8] P. F. Onyon, in *Techniques of Polymer Characterisation* (P. W. Alle ed.), Butterworths, London, 1959, p. 171.
[9] A. L. McClellan, *Tables of Experimental Dipole Moments,* Freeman San Francisco, 1963.

APPENDIX 11b

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THE FORMATION OF TRI-n-BUTYLTIN FLUORIDE FROM TETRAFLUOROHYDROQUINONE

P. DUNN AND D. OLDFIELD

Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, Melbourne (Australia)

(Received December 11th, 1969; in revised form January 22nd, 1970)

SUMMARY

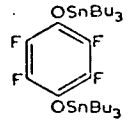
Reaction of tetrafluorohydroquinone with tri-n-butyltin chloride or bis(tri-n-butyltin) oxide has been found to produce tri-n-butyltin fluoride.

INTRODUCTION

The conventional preparation of organotin fluorides is from silver fluoride and the appropriate organotin chloride[1]. It has previously been shown in these laboratories that heating solid ammonium fluoride with bis(tri-n-butyltin) oxide or tri-n-butyltin chloride leads to the quantitative formation of tri-n-butyltin fluoride[2]. Recently we have refined this technique by dissolving bis(tri-n-butyltin) oxide in toluene and adding an aqueous solution of ammonium fluoride whilst stirring vigorously at room temperature, a method analogous to the interfacial condensation procedure for the preparation of organotin esters[3]. The insoluble tri-n-butyltin fluoride is simply filtered off and recrystallised from methanol in the usual way.

RESULTS AND DISCUSSION

In the course of work involving derivatives of fluorinated phenols, a hexane solution of tri-n-butyltin chloride was added at room temperature and under a nitrogen atmosphere, to a vigorously stirred aqueous solution of tetrafluorohydroquinone neutralized with sodium hydroxide with the intention of obtaining compound (I) below. Evaporation of the hexane layer, after a 5 h reaction period, gave a dark



(I)

brown oil which deposited crystals of tri-n-butyltin fluoride, identified by its melting point, IR spectrum and elemental analysis.

Tri-n-butyltin fluoride was also isolated from the organic layer together with an unidentified dark brown oil, after a hexane solution of tri-n-butyltin chloride was stirred at room temperature for 48 h with an aqueous solution of tetrafluorohydroquinone.

When tetrafluorohydroquinone and bis(tri-n-butyltin) oxide were heated together at 130° in the absence of solvent a dark brown residue and tri-n-butyltin fluoride were again produced.

Several additional points are of interest. Firstly, pentafluorophenol reacted readily with tri-n-butyltin chloride by the interfacial method to give tri-n-butyltin pentafluorophenate[4] and secondly, reaction under the same conditions of a hexane solution of tri-n-butyltin chloride with an aqueous neutralized solution of hydroquinone produced only a dark brown residue. Thirdly an aqueous solution of tetrafluorohydroquinone, containing an excess of NaOH, when shaken in air and reacidified with dilute HCl gave a negative test for fluoride ion with zirconium–alizarin reagent[5]. A similar basic solution of tetrafluorohydroquinone when shaken with a hexane solution of tri-n-butyltin chloride and the aqueous layer reacidified, gave a positive fluoride test.

EXPERIMENTAL

The reaction of tri-n-butyltin chloride with neutralized tetrafluorohydroquinone is typical of the procedure employed.

Sodium hydroxide (0.5 g, 0.0125 mole) in water (50 ml) was added to tetrafluorohydroquinone (1.0 g, 0.0054 mole) in water (100 ml) at 18°, under a nitrogen atmosphere. Tri-n-butyltin chloride (3.5 g, 0.0107 mole) in n-hexane (150 ml) was added to the light pink solution and the mixture was stirred for 5 h at 18°. The organic layer was then separated and washed with water until the washings did not give a positive chloride test with silver nitrate solution. The combined aqueous layers were acidified with dilute HCl, extracted with ether (2 × 150 ml), the extracts combined dried ($MgSO_4$) and the ether distilled to leave a trace of a dark brown oil. The dark red hexane layer was distilled on a steam bath to leave a dark brown oil which deposited white crystals on standing. These were recrystallised from methanol as white crystals of tri-n-butyltin fluoride (0.25 g, 0.00080 mole, 7.5% yield) with correct m.p. and IR spectrum. (Found: C, 46.3; H, 8.6. $C_{12}H_{27}FSn$ calcd.: C, 46.6; H, 8.7%.)

REFERENCES

1 H. H. ANDERSON AND J. A. VASTA, *J. Org. Chem.*, 19 (1954) 1300.
2 P. DUNN AND T. NORRIS, *The Preparation of Organotin Compounds*, Defence Standards Laboratories, Report 269, 1964, Department of Supply, Australia.
3 M. FRANKEL, D. GERTNER, D. WAGNER AND A. ZILKHA, *J. Organometal. Chem.*, 9 (1967) 83.
4 D. OLDFIELD, unpublished results.
5 F. FEIGL, *Spot Tests, Vol. 1, Inorganic Applications*, Elsevier, Amsterdam, 1954, p. 252.

APPENDIX 11C
p.11.16-11.17

Reprinted from

Journal of Organometallic Chemistry, 54 (1973) C11–C12

Preliminary communication

Some reactions of organotin compounds under γ-irradiation

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Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, P.O. Box 50, Ascot Vale, Victoria 3032 (Australia)

(Received April 5th, 1973)

SUMMARY

Reaction of organotin compounds with pentafluorobenzene under the influen of γ-radiation produces organotin fluorides.

Ultraviolet radiation is known to cause stepwise degradation of organotin compounds[1], ultimately to metallic tin, but little has been published about the effects of γ-radiation on these compounds. We now report the preliminary results of some γ-radiation induced reactions between organotin compounds and pentafluorobenzene. The obj of this work was to investigate the preparation of fluoroaromatic-substituted organotin compounds by this technique.

The γ-irradiation of solutions of organotin compounds in hexane or benzene produced trace amounts of the stepwise degradation products, which were detected in the reaction mixture by thin-layer chromatography. Thus tetrabutyltin gave trace amou of tributyltin and dibutyltin compounds and similarly tributyltin chloride gave traces of tetrabutyltin and a dibutyltin compound. The same treatment applied to dibutyltin dichloride produced traces of tetrabutyltin and a tributyltin compound in the resulting solution and a deposit of crystals of stannous chloride (6.6% based on original amount of organotin). Butyltin trichloride gave a tarry residue on irradiation in hexane while bis(tri-n-butyltin) oxide yielded a precipirate of dibutyltin oxide (16.4%).

γ-Irradiation of tetrabutyltin in pentafluorobenzene resulted in a copious precipitate of tributyltin fluoride. After irradiation of a hexane solution containing approximately equimolar amounts of tetrabutyltin and pentafluorobenzene a small amo of insoluble dibutyltin difluoride (0.1%) was separated from the now viscous hexane so tion which gave a precipitate of tributyltin fluoride (7.8%) on dilution with acetone. We have previously shown that tributyltin fluoride produces viscous solutions in hexane[2].

nilarly irradiation of hexabutylditin in pentafluorobenzene yielded small amounts of
utyltin oxide (4.1%) from trace impurities such as water or oxygen and tributyltin
oride (10.6%). A hexane solution of tributyltin chloride and pentafluorobenzene gave
y a precipitate of dibutyltin difluoride (5.8%) with no evidence of tributyltin fluoride
ilst dibutyltin dichloride and pentafluorobenzene in hexane produced a precipitate of
nnous chloride (3.0%) and no tributyltin fluoride or dibutyltin difluoride. An intrac-
le tarry residue resulted from the irradiation of a hexane solution containing butyltin
chloride and pentafluorobenzene but a similar solution containing bis(tributyltin) oxide
l pentafluorobenzene gave only a precipitate of dibutyltin oxide (21.2%).

When tetrabutyltin and perfluoro(dimethylcyclohexane) in hexane were irradiated
recipitate of dibutyltin difluoride (0.4%) in a viscous solution of tributyltin fluoride
6%) was obtained. This suggests that fluorine abstraction under irradiation can occur
h alicyclic as well as with aromatic fluorine compounds.

PERIMENTAL

The irradiations were conducted in Quickfit stoppered glass test tubes under an
nosphere of nitrogen with the reactants (3 mmol of each) dissolved in hexane (5 ml).
e radiation was supplied by a 1500 Curie cobalt-60 source built to the design of the
stralian Atomic Energy Commission giving a dose rate of 1.5 $kJ \cdot kg^{-1} \cdot h^{-1}$, as measured
ferrous sulphate dosimetry. The tubes received a dose in the range 220–285 $kJ \cdot kg^{-1}$.
e temperature of the samples during the irradiation was about 30°. Thin-layer chro-
tography was used to examine all the irradiated solutions using well documented methods
differentiate between mono- di-, tri- and tetraalkyltin compounds[3]. This technique
es not identify the anion present in the solution.

After irradiation all the solutions were centrifuged to remove any precipitate
sent. Acetone (30 ml) was then added to the supernatant solution and any precipitate
oduced was centrifuged, rinsed in acetone, dried and identified by melting point and
rared spectrum. The residual solution and washings were evaporated in a rotary evap-
tor and acetone (30 ml) was then added to the residue and any further precipitate was
ated as before.

After further solvent evaporation, the final residue was confirmed as starting
terial in all cases by its infrared spectrum.

FERENCES

I. Akagi and Y. Sakagami, *Koshu Eiseiin Kenkyu Hokoku*, 20 (1971) 1; *Chem. Abstr.*, 77 (1972) 48591.
. Dunn and D. Oldfield, *J. Macromol. Sci., Chem.*, A4 (1970) 1157.
K. Bürger, *Z. Anal. Chem.*, 192 (1962) 280.

APPENDIX 12 ORGANOTINS IN MARINE APPLICATIONS

12a	A New Concept in Antifouling Rubbers	12.2 - 12.3
12b	A Novel Concept in Marine Antifouling Elastomers. P. DUNN and D. OLDFIELD *Rubb. Ind.*, 9 (1), 34 (1975)	12.4 - 12.13
12c	Coated Timber for Underwater Applications P. DUNN and G.F. SANSOM Report 498. Defence Standards Laboratories, Department of Supply, Melbourne.	12.14 - 12.16
12d	Scanning Electron Micrographs of Timber	12.17
12e	Radiograph of a Borer Infested Timber Panel	12.18

The information presented at Appendix 12a is an unabridged retype of the original minute proposing this new area of activity (MRL reference R3/3/33 dated 23 November, 1970).

APPENDIX 12a

DEPARTMENT OF SUPPLY — INTERNAL MEMORANDUM

TO : DR. OLDFIELD POLYMERS R&D SECTION	REGISTRY USE ONLY
FROM : (Branch or Estab.)	OUR FILE NO. R3/3/33 (folio 9)
REFER : P. DUNN EXT'N. 1757	DATE 23 November, 1970

Your Reference :

Subject : A NEW CONCEPT IN ANTIFOULING RUBBERS

As you are aware we have been interested in borer-resistant organic coatings for timbers and have in progress at JTRU, Clump Point, an immersion trial in seawater to evaluate a number of systems. The trial is designated as JTRU, Trial No. 57.

We have also initiated a new trial on organic coatings for timber containing a number of organotin toxins and this is expected to commence early in 1971. The aim of the trial is to combine antifouling properties of coatings with protection against boring organisms. A joint project is also being undertaken with Paints Group concerning antifouling rubbers containing organotin toxins such as bis(tributyltin) oxide, tributyltin fluoride and tributyltin acetate. We have agreed on an experimental programme and this is now being implemented by Mr. J.M.D. Woodford. A trial on these new rubbers is expected to commence at JTRU, Clump Point early in 1971. Simultaneous trials will also be undertaken at Garden Island, Sydney and Williamstown, Victoria.

In 1962/63, a programme of work was undertaken at DSL to develop vulcanized rubbers with fungal-resistant properties. One of the toxins used was poly(tributyltin methacrylate), added either alone or in solution in dinonyl phthalate. A laboratory report on this work is available which describes the use of poly (TBTM) in SBR, natural rubber, polychloroprene rubber and nitrile rubber. The results indicated that up to 4 parts of the organotin polymer per hundred of rubber could be added without difficulty. The use of polymeric organotin compounds in poly(vinyl chloride) has been described in DSL Reports No.298, "Fungicides for Use with Poly(vinyl chloride) and No.359, "Weathering of Plasticised Poly(vinyl chloride)".

Polymeric organotin compounds are prepared by polymerizing the monomer with organic peroxides. These same peroxides are effective vulcanizing agents for some rubbers. I believe it should be possible to polymerize and covulcanize a blend of formulated rubber polymer and an unsaturated organotin monomer. In this manner the organotin polymer should be linked (or grafted) onto the rubber molecule and should thus have improved resistance to removal by leaching with seawater. It should be possible to incorporate a high percentage of organotin polymer by this means and still produce a vulcanizate with acceptable mechanical properties. Such a vulcanizate could have the properties of an efficient anti-fouling rubber. If the covulcanization process can be developed then the system could be the subject of a patent application. To test the possibility, some limited experimental work using butadiene-acrylonitrile rubber and tributyltin acrylate should be undertaken. The organotin monomer is readily prepared from bis(tributyltin) oxide and acrylic acid according to the paper by Montermoso, Andrews and Marinelli (J. Poly. Sci., 32, 523 (1958). Redistilled monomer should be suitable for covulcanization studies.

A typical formulation based on nitrile rubber is:-

Butakon A3003 (ICI) (medium nitrile rubber)	100
Antioxidant ZMB (Zinc mercapto benzimidazole)	2
Acarb 600, carbon black	10
Dicumyl peroxide, 40% (Dicup 40)	2.5 to 7
Trimethylol propane trimethacrylate (Sartomer liquid resin, SR 350)	0 to 7

Typical cure conditions : 30 min at 160°C

The above formulations should be evaluated both with and without the liquid resin, SR 350 and optimum curing conditions developed. The use of 2,5,10,20 and 30 parts of tributyltin acrylate in the formation should then be investigated. All these formulations can be mixed on the 8 inch x 3 inch Thropp, 2-roll mill and examined on the Monsanto Rheometer. Small quantities of materials only would be involved.

Providing a satisfactory system can be developed further work will then be undertaken, with the final possibility of arranging a marine immersion trial to evaluate anti-fouling properties. Other rubbers to be evaluated would include, natural rubber, EPDM rubber, polybutadiene rubber and various blends and formulations. As well as tributyltin acrylate, tributyltin methacrylate and other trialkyl and triaryl organotin unsaturated monomers could also be investigated.

In the first instance however, it is important to ascertain whether the idea of covulcanization and polymerization of a rubber and an organotin unsaturated monomer is possible.

(Signed): P. Dunn
HEAD, POLYMERS GROUP

Reprinted from Rubber Industry Vol 9 No. 1 February 1975

A novel concept in marine antifouling elastomers

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Presented at the Third Australian Rubber Technology Convention organized by the IRI Australasian Section, Terrigal, NSW, 19-21 September 1974

Summary

Elastomeric compositions, incorporating organotin compounds in a novel way, have been developed and trials on these undertaken in temperate and tropical Australian coastal waters to determine their resistance to fouling by marine organisms. The materials have good mechanical properties and on the basis of results to date are expected to resist fouling for a long time.

Introduction

MARINE FOULING CAN be defined as the growth of marine organisms on surfaces immersed in the sea[1]. This growth can take place very rapidly especially in warm waters such as are found around the Australian coastline. The main organisms involved are barnacles, tubeworms, bryozoa, ascidians, hydroids, sponges and weed as well as microfouling species such as diatoms. Fouling usually occurs when the surface, such as the hull of a vessel, is stationary and it thus presents a particularly serious problem for naval vessels. These have to be maintained in a constant state of preparedness in harbour, where favourable conditions for fouling exist. Fouling reduces the speed of a ship, increases its fuel consumption and may adversely effect its handling characteristics. It was estimated a few years ago[2] that a reduction of only 0·15 knots in the speed of a vessel due to fouling would cost $12 000 per annum.

Early attempts to prevent fouling made use of copper sheathing to cover the wooden hulls of vessels. Conventional antifouling paints now in use are based on cuprous oxide which is leached out by the seawater to provide around the vessel a layer of water containing enough copper species to deter settlement of fouling organisms. The minimum release rate[3] to provide protection against fouling should be in the range 50-100 mg/m^2/day.

Organotin toxicants

In the early 1950s van der Kerk[4] showed that organotin compounds of the type Alkyl$_3$SnX were very effective as fungicides. Later the compounds were also found to possess biological activity against many marine fouling organisms. Those that showed the best performance and also had low mammalian toxicity, were tributyltin derivatives such as bis (tributyltin) oxide (TBTO), tributyltin chloride (TBT Cl) and tributyltin acetate (TBT Acetate). When tested in antifouling paints these tributyltin compounds proved to be very effective[5]. A benefit of paint containing organotin compounds is lack of corrosion on metallic surfaces (providing no other metallic pigments are present), and this type is now recommended exclusively for aluminium-hulled yachts[6].

Organotin compounds are known[3] to be more active than cuprous oxide against most fouling organisms. The amount of organotin compound necessary to prevent fouling is usually five to ten times less than that of cuprous oxide as used in conventional antifouling paint. Thus longer foul-free lifetimes could be achieved with organotins if the rate of release into the water could be accurately controlled. This rate is determined by a delicate balance of many factors and depends in part upon the skill of the formulator. Too low a leaching rate will not prevent fouling whilst too high a rate will be wasteful and result in a reduced active lifetime. Also the amount of available toxicant on the hull of a ship is limited by the thickness of the paint film. At present because of such factors it is difficult to extend the effective life of current antifouling paints beyond two years, but longer foul-free lifetimes are required.

Table 1—Formulations of nitrile vulcanizates

	*RT*13	*RT*12	*RT*17
Nitrile rubber	100	100	100
Zinc oxide	5	—	—
Carbon black	10	60	60
Antioxidant	1	2*	2*
Stearic acid	1	—	—
Sulphur	2	—	—
2-Mercaptobenzothiazole disulphide	1·5	—	—
Tetramethyl thiuram monosulphide	0·5	—	—
Trimethylolpropane trimethacrylate	—	3	20
Dicumyl peroxide	—	3	5
TBT Acetate	10	—	—
TBT Acrylate	—	30	187
	131	198	374
Organotin content, % by weight	7·6	15	50
Mould time (90% cure) at 160°C, min	17**	30	30
Tensile strength, M Pa	7·4 (1070 psi)	21·3 (3090 psi)	8·7 (1260 psi)
Elongation at break ,%	310	220	80
Hardness, IRHD	50	64	70
Compression set, %, 24 h at 70°C	11	12	12

*ZMB, zinc mercaptobenzothiazole
**At 150°C

Antifouling elastomers

Providing elastomeric sheets of thickness 1-3 mm could be formulated to contain active organotin compounds then the disadvantages of limited foul-free lifetimes of paints should be overcome due to the greater availability of the toxicant[7]. The sheets could be bonded to underwater surfaces and vulcanizates could also be used for various underwater components, such as cable insulants, gaskets and moulded items. This approach has been investigated in several laboratories following initial work in 1964 by Cardarelli[8] who developed polymeric systems containing a variety of active ingredients which would diffuse slowly into surrounding media, such as fresh or salt water.

As early as 1962, Dunn[9] at Defence Standards Laboratories, showed that organotin compounds could be successfully compounded into several elastomers such as styrene-butadiene (SBR), acrylonitrile-butadiene (nitrile) and natural rubber in order to act as a fungicide. Later Woodford[10], also at DSL, incorporated up to 7·6% by weight, of organotin compounds into several elastomers to investigate their antifouling activity. Immersion trials on these materials were undertaken on a test raft in Sydney Harbour over a two year period[10, 11].

The elastomers used by Woodford were polychloroprene, nitrile and natural rubber, formulated with conventional curing agents, antioxidants and carbon black. The organotin compounds, which were added on the rubber mill prior to

vulcanization at the 2, 5 and 10 phr levels, were bis (tributyltin) oxide (TBTO), a liquid with water solubility of 20-30 mg/l, tributyltin acetate (TBT Acetate) a low melting solid with water solubility of 50 mg/l and tributyltin fluoride (TBTF) a crystalline solid with a very low water solubility of about 1-10 mg/l. In order to study the effect of the elastomer on the rate of release of toxicant, a low level of carbon black filler was used. A typical formulation is given in Table 1 (RT13).

The mechanisms by which toxicants move from a nitrile vulcanizate into seawater are different[11]. TBTO being a liquid dissolves in the vulcanizate and diffuses to the surface and thence into the seawater. TBT Acetate and TBTF on the other hand are leached out by water permeating the vulcanizate and, the low solubility of TBTF is beneficial in preventing too rapid depletion of organotin compound. Certain organotin compounds can retard the cure of elastomers and about 10% by weight of some toxicants is usually the maximum amount that can be incorporated if acceptable mechanical properties are to be retained.

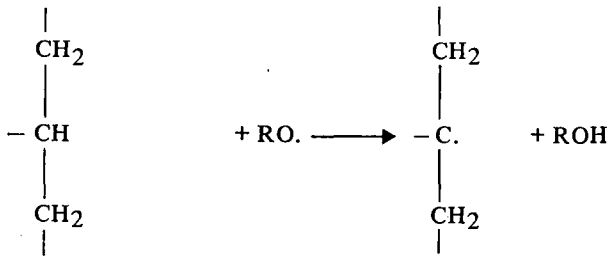
Peroxide-cured antifouling elastomers

In order to increase the amount of toxicant present while retaining good mechanical properties in the vulcanizates, a new concept of incorporating organotin compounds has been developed.

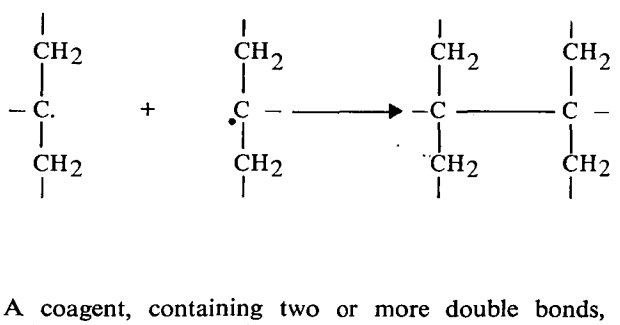
Elastomers may be cured with peroxides (in place of the more conventional sulphur cures) to give vulcanizates with improved heat ageing properties[12]. When a suitable peroxide, such as dicumyl peroxide is heated it decomposes into two radicals:

$$\text{R-O-O-R} \longrightarrow 2\ \text{RO.}$$

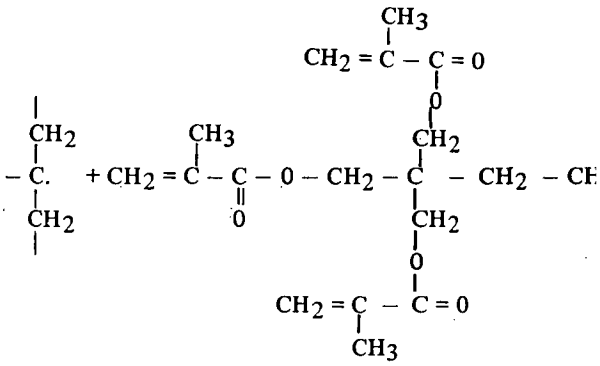
These radicals stabilize themselves by abstracting a hydrogen atom from the polymer chain of the elastomer, hence:

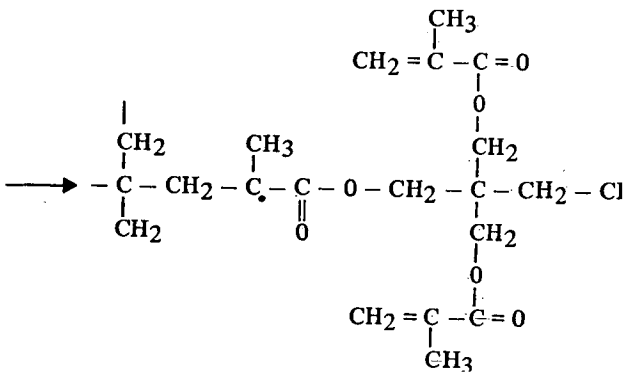


The polymer radicals so formed are able to react with similar radicals to form carbon-carbon crosslinks between the chains.



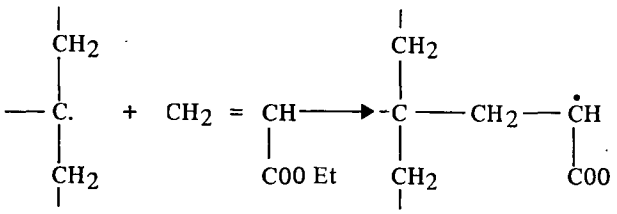
A coagent, containing two or more double bonds, is usually added to peroxide cures to form additional crosslinks[13]. A typical example is trimethylolpropane trimethacrylate, which can react with the polymer radical to prod additional reactive sites.





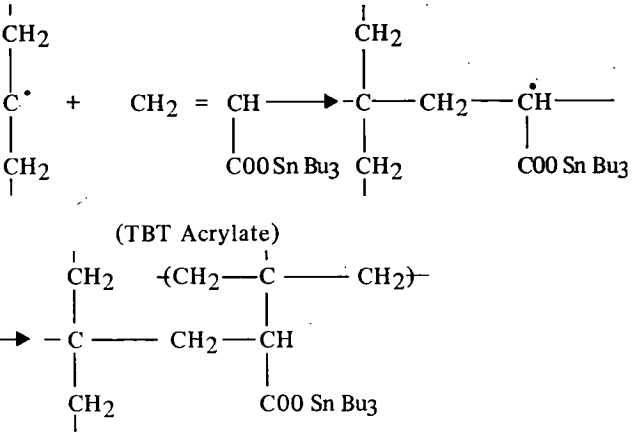
The net result of this grafting reaction is the addition two new reactive sites (at the double bonds) to the polym radical which leads to a greater degree of crosslinking.

In the same way a compound with a single double bo can be grafted onto the polymer chain, thus:



The resulting grafted polymer can then undergo all t previous reactions.

The new concept in antifouling elastomers developed MRL involves adding an unsaturated organotin monom such as tributyltin acrylate (TBT Acrylate), to the mix th curing it with a suitable peroxide. In this case three reactio can occur, namely cross linking of the elastomer (vulcani ation), homopolymerization of the organotin monomer finally covulcanization of the elastomer and the organot compound. For covulcanization the polymer radical c react with TBT Acrylate to form a species that can furth react to form a crosslinked network, thus:



(TBT Acrylate)

The difference between this system and a conventional lphur cured system is that the organotin groups are firmly ound into the network. When seawater diffuses into the lcanizate, reactions occur which cause the release of or-notin groups. This process is expected to be slow and ould prevent rapid release of the toxicant.

A comparison of the different means by which organotin mpounds can be incorporated into vulcanizates is:

$$\text{Rubber} + \text{TBT Acetate} \xrightarrow[\text{cure}]{\text{Sulphur}} \text{Cured rubber} + \text{TBT Acetate (Dispersed)}$$

$$\text{Rubber} + \text{TBT Acrylate (Monomer)} \xrightarrow[\text{cure}]{\text{Peroxide}} \text{Cured rubber} + \text{Poly(TBT Acrylate)}$$

$$\text{Rubber} + \text{Poly(TBT Acrylate)} \xrightarrow[\text{cure}]{\text{Peroxide}} \text{Cured rubber} + \text{Poly(TBT Acrylate)}$$

$$\text{Rubber} + \text{TBT Acrylate (Monomer)} \xrightarrow[\text{cure}]{\text{Peroxide}} \text{Covulcanized rubber/TBT Acrylate}$$

The mechanical properties of the covulcanized system ould be superior to those of the sulphur cured system as e cure is not retarded. The organotin compound would be rmly bound into the polymer network and the release rate the organotin toxicant could thus be controlled. By suit-ly increasing the amount of coagent, it is possible to in-rporate up to 50%, by weight, of TBT Acrylate into fferent types of elastomers. We have examined eleven astomers as well as one plastics material.

esults and discussion

ormulations of test vulcanizates

astomers evaluated included all those likely to be en-untered in modern practice, namely, chlorosulphonated lyethylene, ethylene-propylene terpolymer, ethylene-pro-lene copolymer, natural rubber, styrene-butadiene rubber, yrene-butadiene block copolymer, polybutadiene, nitrile-ly (vinyl chloride) blend, polychloroprene, butyl rubber and trile rubber, as well as polyethylene.

The curing characteristics of each formulation were aluated in a Monsanto rheometer and, all compounds lected for immersion trials were cured at 160° for 30 min ithout reversion. The rheographs for the controls and ganotin-containing mixes were similar. Control vulcanizates, oded RC1-13), which did not contain any organotin com-unds are shown in Table 2, and those containing organotin mpounds, (coded RT1-24), in Table 3. The formulations vulcanizates with the same code number, for example C1 and RT1 were identical except for the addition of

Table 2—Control elastomers

Code	*Elastomer type**	*Abbreviation Used*
RC1	Chlorosulphonated polyethylene	CSM
RC2	Ethylene-propylene terpolymer	EPDM
RC3	Ethylene-propylene copolymer	EPR
RC4	Natural rubber	NR
RC5	Styrene-butadiene copolymer	SBR
RC6	Styrene-butadiene block copolymer	SBS
RC7	Polybutadiene	BR
RC8	Acrylonitrile-butadiene/poly(vinyl chloride) blend	NBR/PVC
RC9	Polychloroprene**	CR
RC10	Polyethylene	PE
RC11	Isobutene-isoprene copolymer (Butyl)***	IIR
RC12	Acrylonitrile-butadiene copolymer (Nitrile)	NBR
RC13	Acrylonitrile-butadiene copolymer****	NBR

*All cured with peroxides as in RT12, Table 1 unless specified otherwise

**Lead oxide cure

***Sulphur cure

****Sulphur cure as in RT13, Table 1

Formulation contained 10 phr of carbon black

Table 3—Vulcanizates containing organotin compounds*

Code	*Elastomer*	*Organotin Compound***	*Filler*	*phr*
RT1	CSM	15% TBT Acrylate	Carbon black	60
RT2	EPDM	" " "	" "	"
RT3	EPR	" " "	" "	"
RT4	NR	" " "	" "	"
RT5	SBR	" " "	" "	"
RT6	SBS	" " "	" "	"
RT7	BR	" " "	" "	"
RT8	NBR/PVC	" " "	" "	"
RT9	CR***	" " "	" "	"
RT10	PE	" " "	Nil	—
RT11	IIR****	15% Poly(TBT Acrylate)	Carbon black	60
RT12	NBR	15% TBT Acrylate	" "	"
RT13	NBR†	7·6% TBT Acetate	" "	10
RT14	NBR	15% TBT Acrylate	Silica	30
RT15	NBR	7·5% TBT Acrylate††	Carbon Black	60
RT16	NBR	30% TBT Acrylate††	" "	"
RT17	NBR	50% TBT Acrylate††	" "	"
RT18	NBR	15% Poly(TBT Acrylate)	" "	"
RT19	NBR	5% TBTO, 10% TBT Acrylate	" "	"
RT20	NBR	5% TBT Acetate, 10% TBT Acrylate	" "	"
RT21	NBR	5% TBTF, 10% TBT Acrylate	" "	"
RT22	NBR	15% TBT Acrylate	$CaCO_3$†††	50
RT23	NBR	" " "	Clay†††	"
RT24	NBR	" " "	NaF†††	"

*Basic formulation as in RT12, Table 1.

**TBT=tributyltin; TBTO=bis(tributyltin) oxide; TBTF=tributyltin fluoride.

***Lead oxide cure+dicumyl peroxide for covulcanization.

****Sulphur cure, no added peroxide.

†Sulphur cure, as in RT13, Table 1.

††Coagent, trimethylolpropane trimethacrylate used with 7·5%, 30% and 50% TBT Acrylate was 3 phr, 3 phr and 20 phr respectively.

†††Carbon black, 10 phr, added as a pigment.

organotin compound to the latter. Vulcanizates RT14-24 were based on the standard nitrile formulation, RT12 (Table 1), with variation of organotin compound type and percentage of filler as shown (Table 3). With the exception of butyl rubber and polychloroprene all were cured with dicumyl peroxide. The presence of TBT Acrylate in the mix did not markedly affect the curing characteristics. Butyl rubber was cured with zinc oxide and sulphur in the presence of prepolymerized TBT Acrylate. Polychloroprene was cured with lead oxide and the formulation containing TBT Acrylate also contained dicumyl peroxide, to polymerize the organotin compound during vulcanization. The formulations were developed following initial work with nitrile elastomer had established that an optimum level of 3 phr of trimethylolpropane trimethacrylate with 30 phr of TBT Acrylate (Table 1, RT12, 15% by weight) was necessary to ensure adequate crosslinking. When the TBT Acrylate content was increased to 187 phr (Table 1, RT17, 50% by weight) the resin needed to be increased to 20 phr.

Properties of test vulcanizates

Generally in the presence of organotin compounds the mechanical properties of the peroxide cured vulcanizates were superior to those for similar sulphur cured vulcanizates. Results shown in Table 1 (RT12 and RT17) are typical.

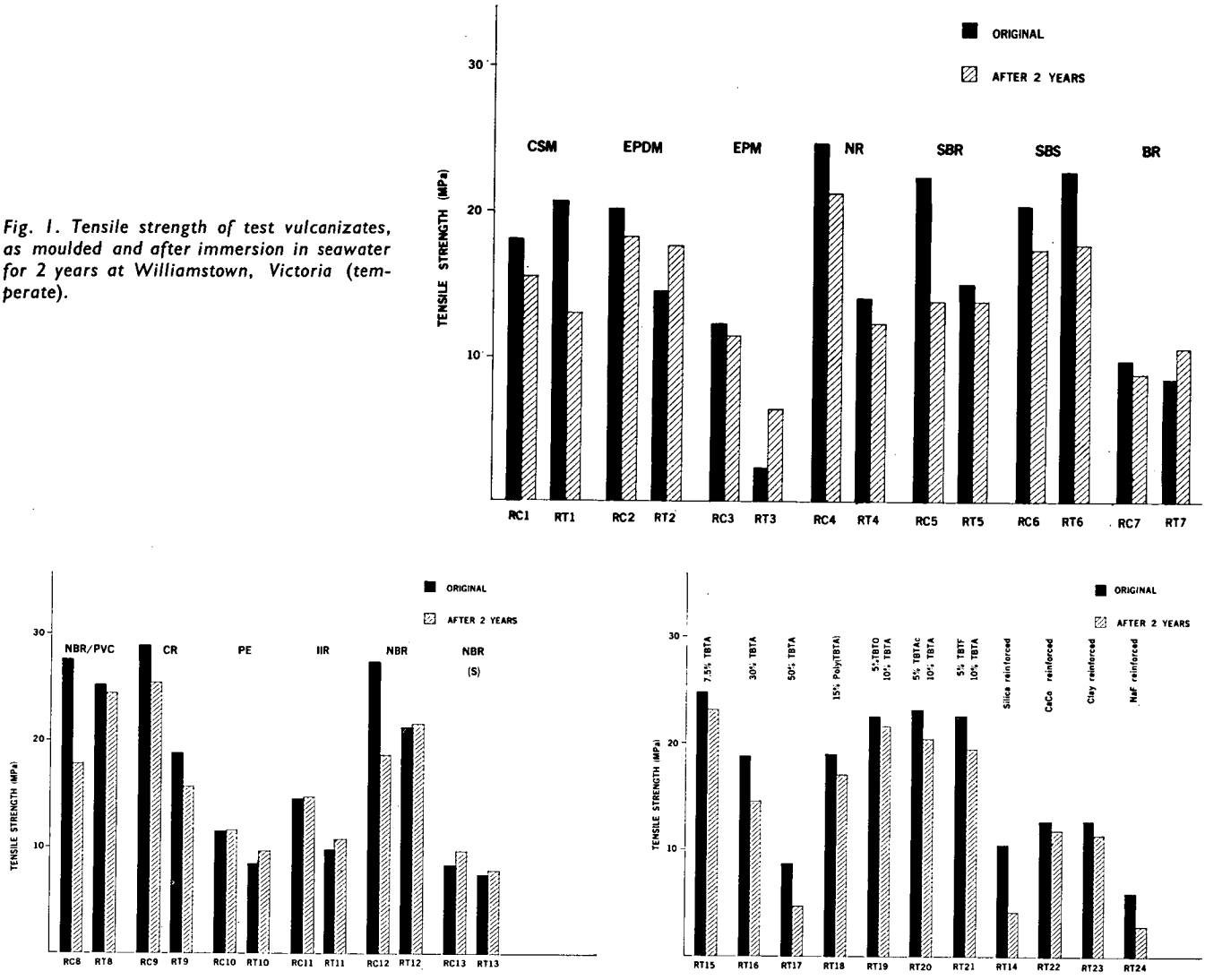


Fig. 1. Tensile strength of test vulcanizates, as moulded and after immersion in seawater for 2 years at Williamstown, Victoria (temperate).

Detailed properties of the vulcanizates, as moulded are given in Figs 1, 2 and 3.

A standard nitrile vulcanizate of the type shown in Table 1 behaved well on ageing for 7 days at 70°C in air and seawater. The original tensile strength (RT12 but containing 50 phr of carbon black) of 12·30 M Pa increased to 21·0 M Pa in air and 14·5 M Pa in seawater. The elongation at break increased from 200% to 250% in air and to 215% in seawater whilst the hardness increased from 60 IRHD to 70 IRHD in air and 69 IRHD in seawater. Weight losses recorded after 7 days at 70°C were 0·6% in air and 0·09% in seawater. Volume swell at 20°C for 24 h in ASTM oil No. 3 was zero and in ASTM fuel B was 26%.

The low compression set value of 12% (Table 1) for vulcanizates containing 15% and 50% by weight, of TBT Acrylate probably indicates that covulcanization had occurred. Had the organotin compound been homopolymerized it would have acted in the rubber as a polymeric plasticizer and the two vulcanizates with markedly different organotin contents would have shown different compression set values. Although mix RT12 contained 15% TBT Acrylate by weight, an ether extract of the vulcanizate in a hot Soxhlet extractor for 8 h contained only 7% residue as compared to 3% from a control vulcanizate without TBT Acrylate. This result gives an indication of the extent to which the organotin compound is incorporated into the vulcanizate, either by covulcanization or as high molecular weight organotin polymer.

The effect of different levels of carbon black on the mechanical properties of vulcanizates containing TBT Acryla was also investigated and results are given in Table 4.

Effect of seawater immersion on properties

Vulcanizates (225 mm × 125 mm × 1·9 mm) mounted aluminium frames were immersed at Williamstown Nav Dockyard, Victoria (temperate site) and at the Joint Tropic Research Unit, Clump Point, North Queensland (tropic site). The set at Williamstown was placed in tanks throug which fresh seawater was continually pumped. The other s was suspended 1 m below the surface from a raft moored i 8 m of water. The mechanical properties of the vulcanizat originally and after 2 years immersion at Williamstown a given in Figs 1, 2 and 3. The data presented should enab vulcanizates to be selected for specific applications.

During immersion for two years, changes in the tensi strength of vulcanizates ranged between 1% and 40%.

Table 4—Effect of carbon black content on mechanical properties

Curing system Organotin compound	Sulphur* TBT Acetate	Peroxide† TBT Acrylate	Peroxide† TBT Acrylate	Peroxide TBT Acrylate
Organotin content, %	7·6	15	15	15
Carbon black, phr	10	10	50	60
Tensile strength, M Pa	7·4	6·2	12·3	21·3
Elongation at break, %	310	260	200	220
Hardness, IRHD	50	42	60	64
Compression set, %, 24 h at 70°C	11	6·9	7·5	12

*Compound RT13, Table 1.

†Compound RT12, Table 1, with modified carbon black content.

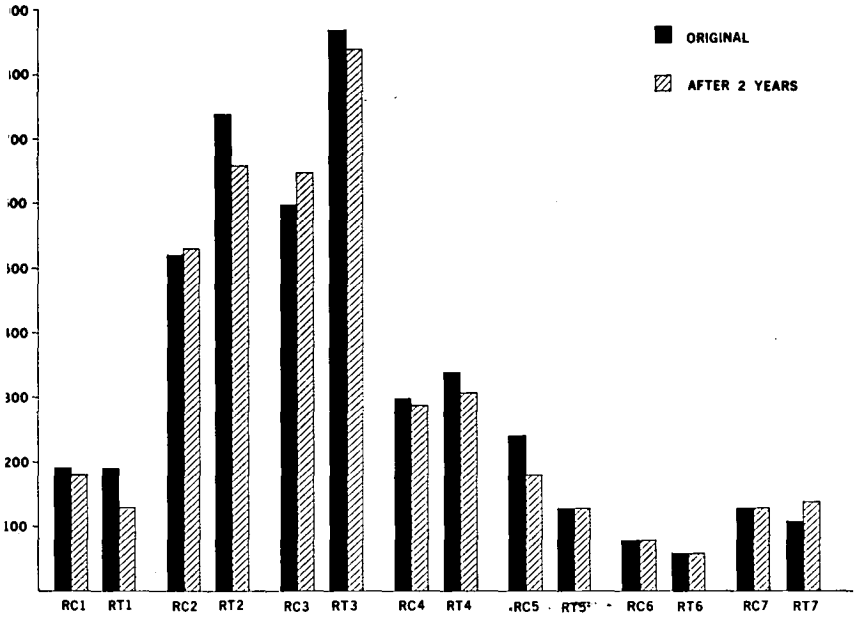
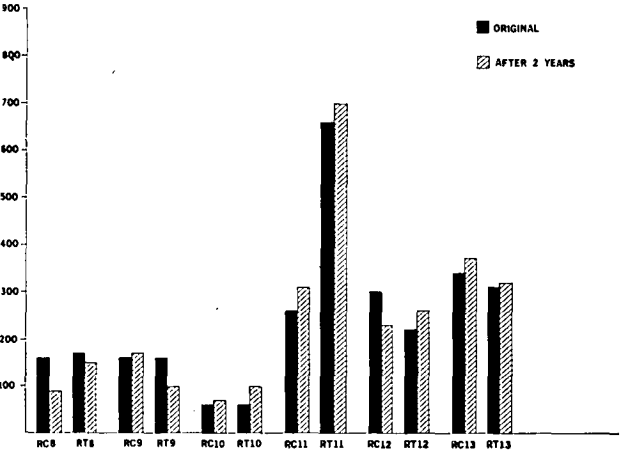
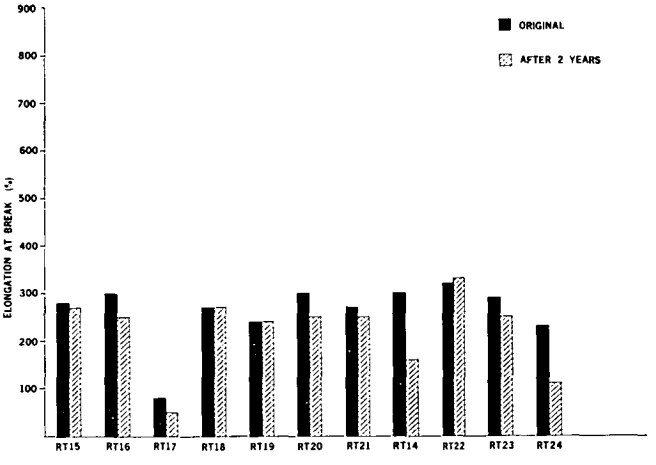


Fig. 2. Elongation at break of test vulcanizates as moulded and after immersion in seawater for 2 years at Williamstown, Victoria (temperate).





ıny cases the vulcanizates containing organotin showed a aller change than the equivalent controls. The same trends o applied to the elongation at break and hardness values the specimens.

The low value of 1·5% change in the tensile strength of e nitrile vulcanizate (RT12) containing TBT Acrylate is of erest compared to a 32% loss in tensile strength for the uivalent control (RC12). After 2 years immersion this lcanizate (RT12) containing organotin had a higher tensile ength and greater elongation at break than the control. is justified the selection of nitrile rubber as the matrix ed to investigate the effects of changes in filler or organotin mpound.

The silica reinforced vulcanizate RT14 (Table 3) showed a ge reduction (60%) in tensile strength during immersion obably due to the effect of water on the silica-elastomer nd. Incorporation of 7·5%, 30% and 50% of TBT Acrye into nitrile vulcanizates (RT15, 16 and 17 respectively) owed that different amounts of toxicant could be used thout seriously degrading mechanical properties. These lcanizates were still useful materials after marine immern for 2 years. Incorporation of pre-polymerized TBT Acrye also gave a vulcanizate (RT18) whose elongation at eak and hardness values were little affected by immersion. A mixed toxicant system, comprising 5% by weight, of an ganotin compound such as TBTO, TBT Acetate or TBTF and 10% by weight of TBT Acrylate, was used in RT19-21 respectively. The mechanical properties of these vulcanizates were excellent and were not significantly affected by immersion. An initial high release rate of the oxide, acetate or fluoride, followed by a more gradual release from the acrylate-based toxicant could be advantageous in some highly active fouling situations.

Replacement of 50 phr of the carbon black with calcium carbonate or clay gave vulcanizates (RT22 and 23) with properties sufficiently high for many purposes. They were only slightly affected by marine immersion in contrast to the silica-reinforced vulcanizate (RT14). A soluble filler, sodium fluoride, was used (RT24) to investigate water permeation into the vulcanizate and subsequent leaching out of filler. This vulcanizate rapidly developed a cellular structure and swelled to about double its original size. Thus nitrile vulcanizates have a degree of water permeability sufficient to leach out soluble toxicants or to enable removal of reaction products.

Organotin content of vulcanizates

The residual organotin content of the vulcanizates after various immersion periods was measured by X-ray fluorescence spectroscopy (XRF)[14]. In this non-destructive technique a small disc of the sample was bombarded by a beam of X-rays and the resultant radiation analysed for wavelengths character-

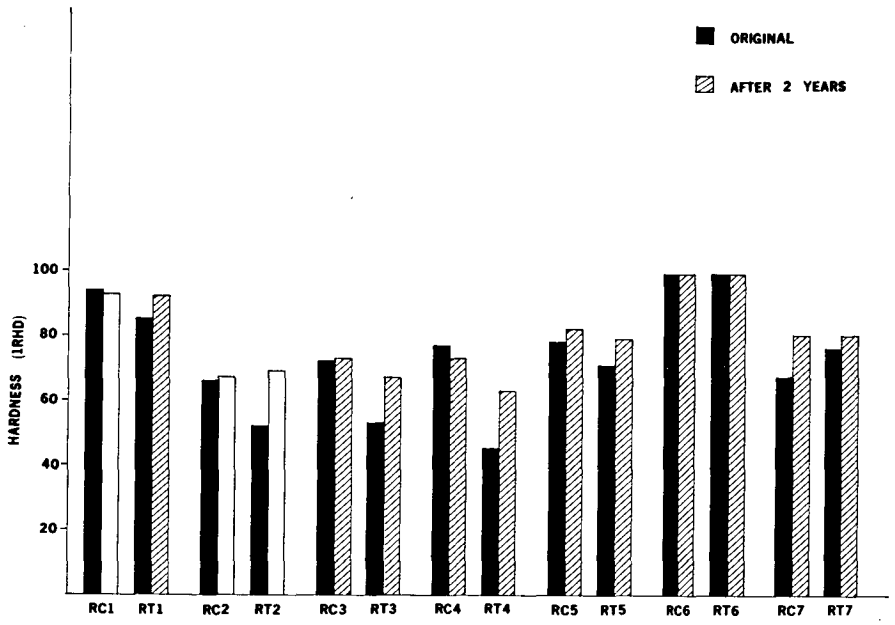
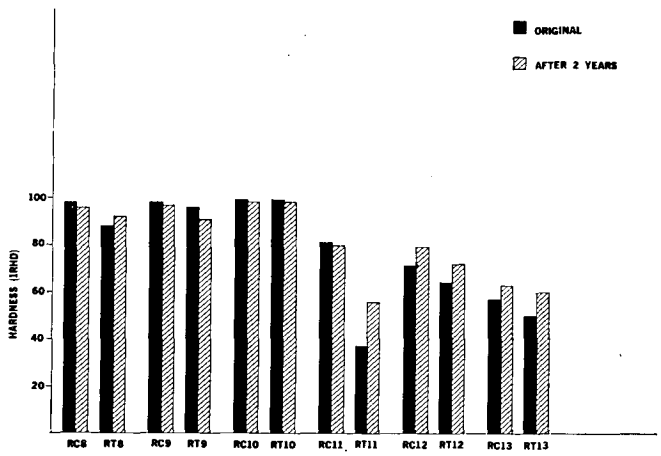
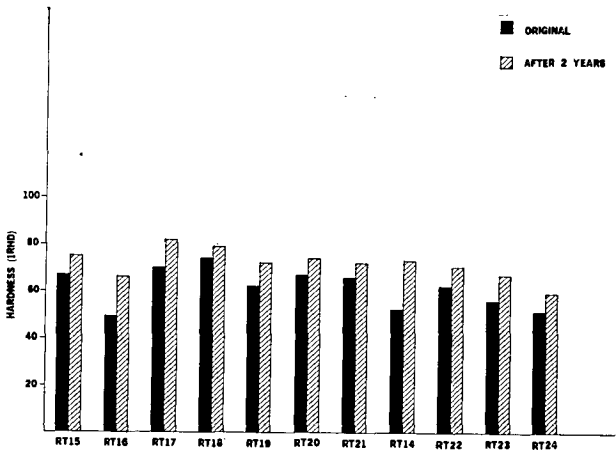


Fig. 3. Hardness (IRHD) of test vulcaniza as moulded and after immersion in seaw for 2 years at Williamstown, Victoria, (t perate).





istically emitted by tin. The results (Table 5) show a slow decrease in organotin content during immersion for 24 months at Williamstown and 12 months at Clump Point, North Queensland. The two nitrile vulcanizates, RT12 (peroxide cured and containing 15% covulcanized TBT Acrylate) and RT13 (sulphur cured and containing 7·6% TBT Acetate) can be compared. The residual organotin in RT12 was reduced to 14% and 11% after immersion for 12 and 14 months respectively at Williamstown and to 8% after immersion at Clump Point for 12 months. With RT13 the organotin content was reduced to 4% and 2% after immersion at Williamstown for 12 and 24 months respectively and to 1% after immersion at Clump Point for 12 months. The accuracy of the analysis is about $\pm$ 10% of the values quoted. The results indicate that curing with peroxides is an effective method of reducing the release rates of specific organotin compounds, thereby increasing the antifouling lifetime of vulcanizates.

The decrease in organotin content of four nitrile vulcanizates containing initially 7·5%, 15%, 30% and 50% by weight, of TBT Acrylate is shown in Fig 4. Trends indicated by the graphs suggest that the organotin content of all these vulcanizates will be reduced to zero after immersion for 6-7 years. The graphs indicate that for a particular vulcanizate the release rate of organotin compound is nearly constant during immersion and for the four vulcanizates is propor-

Table 5—Residual organotin content of vulcanizates after immersion

	Williamstown (temperate)					*Clump Point (tropical)*	
		1 year immersion		*2 year immersion*		*1 year immersio*	
*Code**	*Original Organotin Content %*	*Residual Organotin Content, %*	*Release Rate over 1 yr mg/m²/ day*	*Residual Organotin Content, %*	*Release Rate over 2 yr mg/m²/ day*	*Residual Organotin Content, %*	*Relea Rat over 1 mg/m²/ day*
RT1	15	13	90	10	120	7	370
RT2	15	13	90	12	70	12	140
RT3	15	13	90	9	140	12	140
RT4	15	11	180	11	90	10	230
RT5	15	13	90	11	90	10	230
RT6	15	13	90	14	20	17	0
RT7	15	13	90	12	70	15	0
RT8	15	15	0	14	20	17	0
RT10	15	17	0	15	0	10	230
RT11	15	12	140	10	120	10	230
RT12	15	14	45	11	90	8	330
RT13	7·6	4	162	2	130	1	310
RT14	15	16	0	13	50	13	90
RT15	7·5	7	30	7	10	5	120
RT16	30	26	180	19	260	32	0
RT17	50	29	900	35	350	†	†
RT18	15	13	90	13	50	17	0
RT19	15	14	45	14	20	12	140
RT20	15	11	180	10	120	9	280
RT21	15	13	90	13	50	13	90
RT22	15	11	180	8	160	12	140
RT23	15	13	90	12	70	9	330
RT24	15	12	140	4	260	†	†

*RT9 could not be analysed by XRF due to the lead curing agent.
†Panels RT17 and RT24 at Clump Point were lost in a storm.

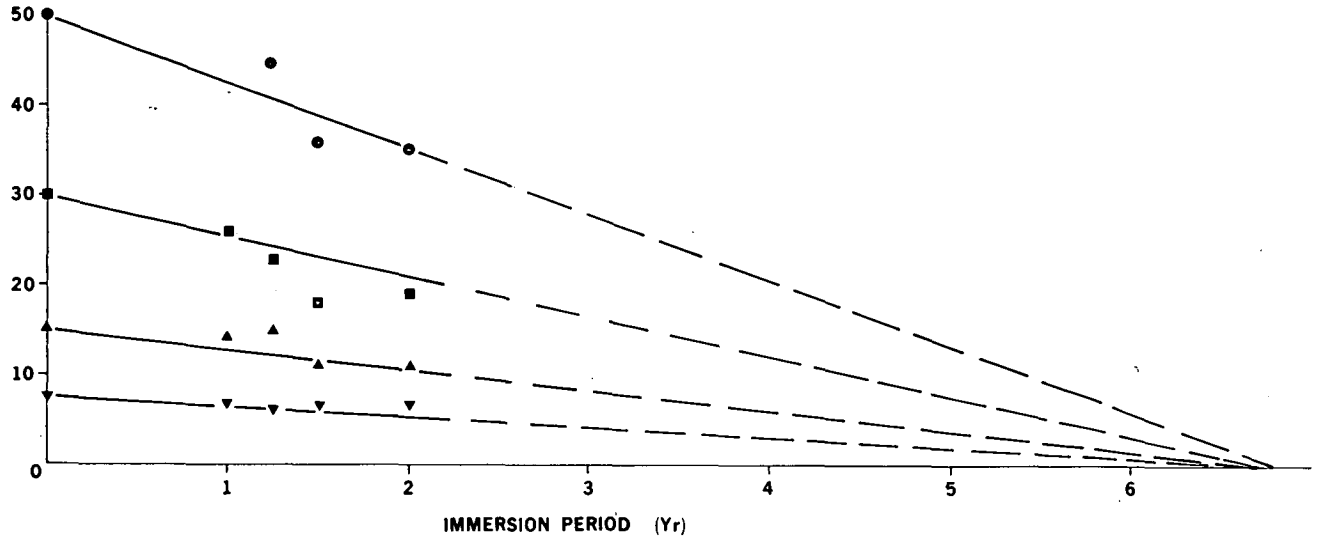


Fig. 4. Residual organotin content of four nitrile vulcanizates after immersion in seawater at Williamstown, Victoria (temperate).

nal to the initial concentration of TBT Acrylate. A know-
ge of the release rates of the systems studied (Table 5),
ould enable vulcanizates to be designed which would have
fficiently high release rates to prevent fouling for an ex-
ded period. Most of the vulcanizates had release rates
er two years greater than that which has been quoted as
minimum necessary[3] to prevent fouling (10 mg/m²/day).
value for the minimum release rate necessary to prevent
uling in Australian waters could result from further studies
ned at correlating antifouling performance with release
es. The higher water temperatures at clump point (24°-
°C) compared to Williamstown (11°-23°C) generally resul-
l in higher release rates of organotin compound at the
mer site. This could be beneficial as marine fouling is
ually more severe in tropical waters.

For comparison a sample of a commercial antifouling
lychloroprene vulcanizate which originally contained 6%
ganotin compound[8] had a residual organotin content of
ly 2% after immersion for 8 months at Clump Point.

ntifouling performance

uring immersion at Williamstown (temperate) in tanks
olific weed growth occurred on the control vulcanizates
ilst those containing organotin became covered only with
coating of slime which was easily washed off with a jet of
ter. In the second summer, at Williamstown, during the
aviest fouling season a dense mat of green weed also grew
the surface of the water in the tanks. This inhibited further
owth of weed on the test specimens and accounted for their
atively clean appearance on withdrawal at the end of the
o years. No barnacles were present as these do not grow
idily at this exposure site.

The extent of fouling present on specimens immersed at
ump Point (tropical) was assessed after 12 and 14 months
able 6). The control vulcanizates (RC series) were all
avily fouled by barnacles and other organisms after 12
onths. An apparent reduction in the amount of weed
esent on the specimens in the two months between in-
ections is possibly due to normal environmental factors,
d could illustrate the dynamic nature of the fouling com-
unity.

The two vulcanizates with the widest range of fouling were
lorosulphonated polyethylene (RT1) and styrene-butadiene
ock copolymer (RT6). In both cases however, the extent
barnacle growth was low. Other vulcanizates, which were
ghtly fouled by barnacles after 12 months, were natural rubber (RT4), styrene-butadiene rubber (RT5), nitrile-poly (vinyl chloride) blend (RT8), nitrile rubber containing pre-polymerized poly (TBT Acrylate) (RT18) and nitrile rubber reinforced with clay (RT23). All other specimens containing organotin compounds were free of barnacles but some were fouled by weed.

After immersion for 14 months, the extent of barnacle growth on the specimens had not changed significantly. However one or two barnacles had settled on vulcanizates that were not fouled after twelve months. These vulcanizates were polybutadiene (RT7), nitrile rubber containing 15% TBT Acrylate (RT12) and nitrile rubber containing 7·5% TBT Acrylate (RT15).

An apparent correlation is possible between rate of release of organotin compound during 12 months immersion at Clump Point (Table 5) and antifouling performance (Table 6). Four of the five vulcanizates which had very low release rates, namely RT6, RT7, RT8, RT16 and R18, all developed slight barnacle growth during 14 months immersion—the exception was RT16. Release rates give no indication whether

Table 6—Extent of marine fouling on panels immersed at Clump point

	*Fouling oranisms**									
Code†	*Barnacles*		*Bryozoa*		*Green weed*		*Brown or red weed*		*Slime*	
RT1	S	(S)		(S)	S	(M)	S	(M)	H	(M)
RT2							S		M	(H)
RT3						(S)	S		M	(H)
RT4	S		S			(S)	S		H	(H)
RT5	S	(S)					S		M	(H)
RT6	S	(S)	M	(H)	S		M	(M)	M	(M)
RT7		(S)					M		H	(M)
RT8	S	(S)							H	(H)
RT9							S		S	(M)
RT10		(S)					S		H	(H)
RT11							M		M	(H)
RT12		(S)							H	(M)
RT13									M	(M)
RT14									H	(H)
RT15		(S)					S		H	(H)
RT16							H		S	(H)
RT18	S	(S)					S		H	(H)
RT19		(S)					S		M	(H)
RT20							M		S	(H)
RT21							S		M	(H)
RT22							S		M	(H)
RT23							S		H	(H)

*Extent of fouling cover; Slight (S)= 1 to 9% of panel area; Moderate (M)= 10 to 30% of panel area; Heavy (H)=over 30% of panel area. First column in each case after 12 months immersion, second column (in parentheses) after 14 months.

†Panels RT17 and RT24 were lost in a storm.

the organotin compound is lost at a constant rate or initially very rapidly followed by a period of slow release. Vulcanizate RT1 lost a large amount of organotin compound and was slightly fouled by a wide range of organisms after 12 months. In this case a rapid initial loss followed by very slow release may have taken place. Local inhomogeneities in the vulcanizates could also lead to variations in the values of the residual organotin content.

In those cases where an apparently high release rate of organotin and fouling had also occurred, further detailed studies on the mechanism of release of toxicant needs to be undertaken. Thus in all instances where the organotin compound was tightly bound into the vulcanizate, as evidenced by the low release rate, some fouling by barnacles occurred.

In the present immersion trial the sulphur-cured nitrile rubbers (Tables 2 and 3, RC13 and RT13) contained only 10 phr carbon black and RT13 in addition contained 10 phr, (about 7·6% by weight) of TBT Acetate. These two vulcanizates were comparable to two vulcanizates used in an earlier trial by Woodford[10]. This enables the antifouling activity of the vulcanizates in the two series to be correlated, and this work is continuing.

Experimental

The compounding materials used were commercial products obtained from recognized suppliers. Details are given in the Appendix. Other compounding materials comparable in chemical composition and activity should prove to be equally satisfactory.

All of the formulations were processed on conventional rubber compounding equipment. Whenever possible, masterbatches were mixed on a 500 mm × 250 mm variable speed two-roll mill, while hot mixing and final compounding were carried out on a 300 mm × 150 mm mill. Test sheets were vulcanized in a single cavity mould in an electrically-heated press.

TBT Acrylate was prepared from bis(tributyltin oxide) and acrylic acid by a recognized procedure[15] and was recrystallised twice from n-hexane before use. Other organotin compounds were prepared by established methods[16]. Standard testing equipment and methods were used [17-20].

A Phillips model 1540 X-ray fluorescence spectrometer was used to measure the tin content of the specimens. To calibrate the measurements the peak height corresponding to the intensity of the tin emission was plotted against the original tin content for the unexposed vulcanizates RT15, RT12, RT16 and RT17 which contained originally 7·5%, 15%, 30% and 50% TBT Acrylate respectively. This straight line graph was then used to determine the tin content, and hence the organotin content, in specimens returned from marine immersion.

Conclusions

Tributyltin acrylate can be incorporated into elastomers and the compound then cured with peroxides to give vulcanizates having excellent mechanical properties which are substantially retained after long periods of marine immersion. The vulcanizates are highly effective in preventing growth of marine fouling on their surfaces. Those of particular interest were based on chlorosulphonated polyethylene, ethylene-propylene terpolymer, natural rubber, styrene-butadiene, polybutadiene, nitrile-poly(vinyl chloride), polychloroprene, and nitrile rubber. Although carbon black reinforced vulcanizates are preferred, satisfactory properties were obtained when either calcium carbonate or clay was used as a non-black filler. The most promising systems investigated would be expected to have superior performance to that previously reported for antifouling elastomers.

Acknowledgements

Thanks are due to Officer-in-Charge, JTRU, Innisfail for arranging the exposure of samples and the issue of t reports, and to Mr I G McDonald, Metals Analysis Gro DSL for the tin analyses.

References

1. Phillip, A T, Prog Org Coat, 2 159 (1973/74).
2. Evans, C J, Tin and its Uses, No 85 3 (1970).
3. Bennett, R F and Zedler, R J, J Oil Col Chem Assoc, 49 928 (1966); M S M, Ind Eng Chem Prod Res Dev, 3 226 (1964).
4. Luijten, J G A, in Organotin Compounds ed Sawyer, A K, Marcel Del New York, p 940 (1972).
5. Zedler, R J, Metal Finishing, 60 (12) 57 (1962).
6. Anon, Tin and its Uses, No 78 4 (1968).
7. Ochiltree, B C, Antifouling Elastomeric Compositions. Report 2 Admiralty Materials Laboratory. Department of Defence (Navy). Hc Heath, Poole, UK (1972).
8. Cardarelli, N F, Tin and its Uses, No 93 16 (1972).
9. Dunn, P, Elastomeric and Fungicidal Organotin Compounds. F presented at 36th Congress ANZAAS, Sydney. Defence Standards Lat tories, Department of Supply (1962).
10. Woodford, J M D, Underwater Marine Coatings Part II. Marine Bio Rubbers Containing Organotin Toxics. Report 496. Defence Stanc Laboratories, Department of Supply, Maribyrnong, Victoria (1972).
11. De Forest, A, Pettis, R W and Phillip, A T, Underwater Marine Coat A Detailed Examination of Elastomeric Antifouling Materials Marine Immersion. Report 589. Defence Standards Laboratories, De ment of Supply, Maribyrnong, Victoria (1974).
12. Loan, L D, Rubb Chem Technol, 40 149 (1967).
13. Pickup, B, Peroxide/Coagent Vulcanization. Rubber Division Lit Bibliography No 38. University of Akron, Ohio, USA (1970).
14. Driscoll, C and Freiman, A, J Paint Technol, 42 521 (1970).
15. Montermoso, J C, Andrews, T M and Marinelli, L P, J Polym Sci, 32 (1958).
16. Dunn, P and Norris, T, The Preparation of Organotin Compounds. Re 269. Defence Standards Laboratories, Department of Supply, Maribyrn Victoria (1964).
17. Determination of Tensile Stress-Strain Properties. BS903: Part A2. Bi Standards Institution, London (1971).
18. International Hardness of Vulcanized Rubber. ASTM D1415-68. Amer Society of Testing and Materials, Philadelphia, Pa.
19. Compression Set of Vulcanized Rubber. ASTM D395-69. Method B, 2.
20. Change in Properties of Elastomeric Vulcanizates Resulting from Immer in Liquids. ASTM D471-72.

Appendix

Compounding materials

Material	*Trade Name*	*Supplier*
Chlorosulphonated polyethylene	'Hypalon' 40	Du Pont Inc.
Ethylene-propylene terolymer	'Nordel' 1440	Du Pont Inc.
Ethylene-propylene rubber	'Dutral' N	Montecatini Edison
Natural rubber	Smoked sheet No 1	Malaysian Rubber Bureau
Styrene-butadiene rubber	'Austrapol' 1502	Australian Synthetic Rubber Co.
Styrene-butadiene block copolymer	'Solprene' 406	Phillips Chemical Co
Polybutadiene	'Austrapol' 1220	Australian Synthetic Rubber Co.
Nitrile rubber/poly(vinyl chloride)	'Butakon' AC 5502	ICI Aust Ltd.
Polychloroprene	'Neoprene' AC Soft	Du Pont Inc.
Polyethylene	XP 219	Union Carbide Aust
Butyl rubber	Butyl 600	Polysar Ltd.
Nitrile rubber	'Butakon' A 3003	ICI Aust Ltd.
Dicumyl peroxide (40% active)	Dicup 40C	Hercules Powder Co.
Trimethylolpropane trimethacrylate	SR 350	Sartomer Resin Inc.
Hydrated silica	'Neosyl' standard	Crossfield Pty Ltd.
Calcium carbonate	'Winnofil' S	ICI Aust Ltd.
Clay	Kaolin 37	ACIM
Sulphur, coated	Sulphur MC	Aubrey Wark.
Zinc mercaptobenzothiazole	ZMB	Bayer Australia Ltd.
Antioxidant	Nonox B	ICI Aust Ltd.
Tetramethyl thiuram monosulphide	'Vulcafor' MS	ICI Aust Ltd.
2-Mercaptobenzothiazole disulphide	'Vulcafor' MBTS	ICI Aust Ltd.
Carbon black	'Acarb' 600	Australian Carbon Black Pty Ltd.
Bis(tributyltin) oxide	TBTO	Osta Chemicals Ltd.

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REPORT 498

COATED TIMBER FOR UNDERWATER APPLICATIONS

P. Dunn and G. F. Sansom

SUMMARY

The protection of timber (West African mahogany, **Khaya ivorensis**) when used in the underwater environment has been investigated. Trials were undertaken in the sea off Clump Point, North Queensland, to determine the resistance of timber coated with reinforced and unreinforced organic materials, to attack by shipworms. Eleven coating systems, all of potential practical value, were evaluated. Some organotin toxicants were incorporated into some timber and coatings in order to assess their effects, if any, on marine growths and organisms.

A non-destructive radiographic technique was used to examine exposed panels for evidence of attack by shipworms. The ability of barnacles to record characteristic imprints on a specific type of coating, was also observed. Of the coatings examined, four materials showed excellent performance, following marine immersion for periods of up to thirty-six months.

MARCH, 1972

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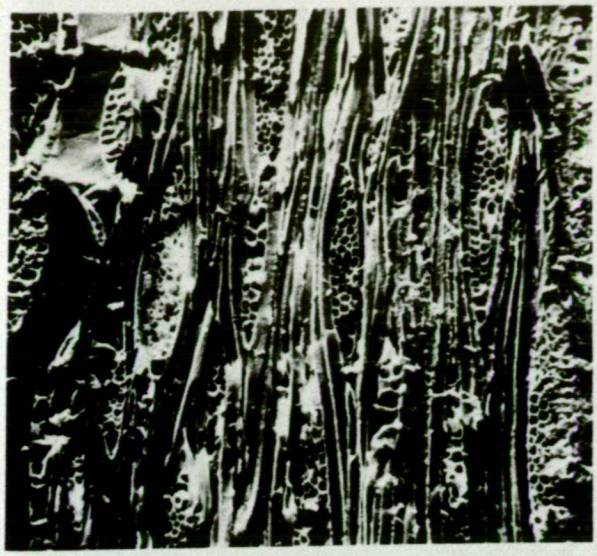
NOTE - RE MATERIALS

Formulations of the coating materials mentioned in this report are available to Defence Group Departments, on application to Defence Standards Laboratories.



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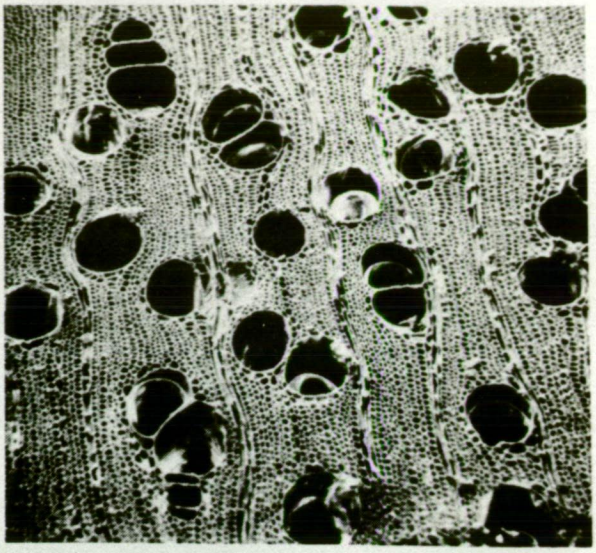

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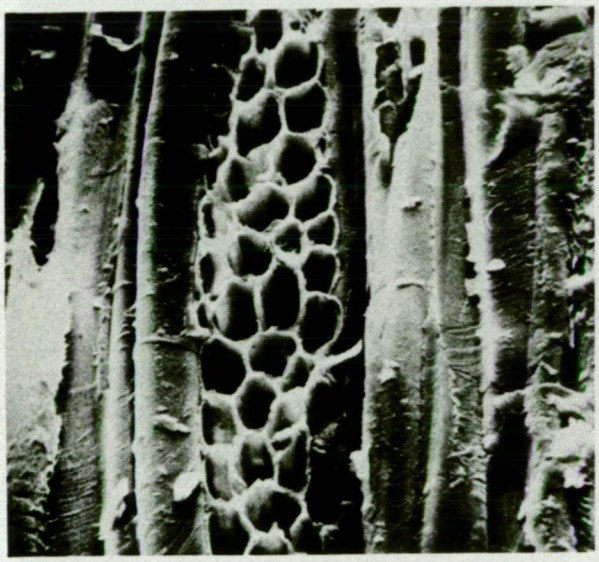

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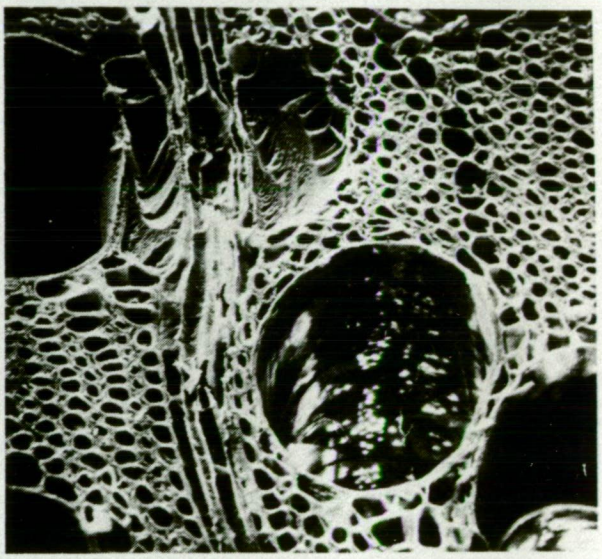

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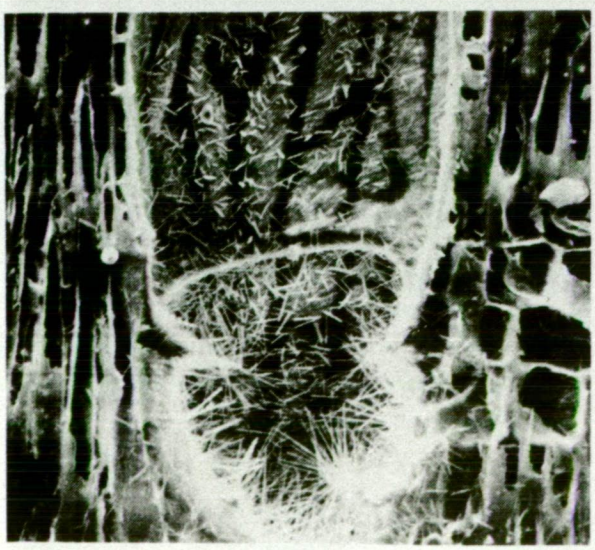

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FIG. 1 - Scanning electron micrographs of longitudinal sections (LS) and transverse sections (TS) of Khaya ivorensis timber. The upper four micrographs are of unimpregnated timber. The two lower micrographs show crystals of tributyltin fluoride formed in situ in vessels in the timber (lower left) and projecting through pits in the vessel wall (lower right).

Appendix 12e - Radiograph of a panel of *Khaya ivorensis* coated with white acrylic latex. After immersion for 36 months the coating had failed and borers had infested the panel(mag., X0.9).

APPENDIX 13 ORGANOTINS AS FUNGICIDES FOR RUBBERS

13a Antifungal Sealing Rings - A New Approach
P. DUNN and D. OLDFIELD
Plast. and Rubb. Mats and Applns,
3, No. 3, 87 (1978). 13.2 - 13.11

ADDENDUM TO APPENDIX 13a

A display entitled, *Antifungal Sealing Rings* will be presented at the FIRST AUSTRALIAN TECHNOLOGY RESOURCES EXCHANGE FAIR, TRX 79, to be held in Sydney, Australia, 27-30 March, 1979. TRX 79 is being organised by the Australian Innovation Corporation Limited, which is an undertaking sponsored by selected major Australian industries and financially supported by the Australian Government.

The aim of TRX 79 is to extend the market reach of Australian-originated applied research and advanced technology, by promoting its transfer to local industry. An invited audience, drawn from industry, commerce and government and academic institutions, will view the Fair.

30 January 1979

Antifungal sealing rings: a new approach

P. Dunn and D. Oldfield
Materials Research Laboratories, Department of Defence, Victoria 3032, Australia

Abstract: A new approach has been used both in the laboratory and in field trials, to study the development and performance of special vulcanizates used in sealing applications. Conventional, monomeric fungicides have been replaced by polymeric organotin compounds covulcanized into the rubber network. Polychloroprene, acrylonitrile-butadiene rubber and ethylene-propylene terpolymer are three rubbers commonly used in military equipment and these have been shown to covulcanize with tributyltin acrylate in the presence of peroxides to give vulcanizates with a powerful and long-lasting fungicidal action. These rubbers have been evaluated by the use of O-rings to form sealed cavities with ten different materials (two metals, seven plastics and glass), in specially designed assemblies. Trials held over 3 years in adverse environments have confirmed that the rubbers are compatible with the sheet materials; that they can be formed into efficient sealing products that will prevent fungal growth; that they have good performance characteristics; and that they do not degrade the optical qualities of transparent materials. These rubbers should have applications in military, industrial and commercial equipment.

Introduction

uring World War II and the Vietnam war, fighting on a ge scale using modern military equipment occurred over vide range of environmental conditions. Equipment losses d failures in adverse environments due to corrosion, crobiological attack, hydrolysis and actinic degradation ere enormous.

In particular, sensitive optical and electronic military uipment was rapidly rendered unserviceable by the growth micro-organisms such as fungi. This problem is still rious in tropical areas and usually results in the use of aborate and costly sealing procedures. Upsher[1] has described some of the problems associated with microbial tack on materials.

A common method of sealing sophisticated military, dustrial and commercial equipment is by the use of O-rings d similar types of seals. These are of value only if they n be shown to effectively prevent the ingress of fungal owths. Fungicides are often incorporated into these rubrs but usually have only limited lifetimes because of their pletion by hydrolysis, leaching, blooming or evaporation om the rubber surface. In addition, many of the fungicides ntain heavy metals such as copper and mercury and these ten promote deterioration of substrate materials. Chlorine-ntaining fungicides are prone to cause corrosion of, and hesion to, metallic components[2].

Fungicides based on organotin compounds are usually ee from many of these disadvantages[3], but may still bloom the surface of the rubber. By means of a modification of system developed at the Materials Research Laboratories prevent the growth of marine fouling on underwater surces[4], elastomeric vulcanizates have been produced which ve long-term fungicidal properties and which can be used sealing applications. Leading references to earlier work the use of organotins in rubber may be found in previous blications[4]. In addition, many reports on the selection of itable elastomers and the use of O-rings are available[5–9].

The main advantage of this system is that it produces high-quality, peroxide-cured vulcanizates with the fungicide bound into the rubber matrix. The mechanical properties of the vulcanizates are not degraded by the incorporation of the fungicide, as can occur when using simple organotin compounds, such as bis (tributyltin) oxide, in sulphur-cured rubbers[4], and, furthermore, these properties are retained over a long period despite exposure to adverse environments. The vulcanizates also remain free from surface bloom of fungicide or other compounding ingredients.

2 Organotin fungicides

Van der Kerk[10] showed that organotin compounds of the type $Alkyl_3SnX$ were very effective fungicides. Commercially used materials include triphenyl and tributyltin oxide, chloride, fluoride and acetate. Triphenyltin acetate, for example, is marketed as a 20% active water-wettable powder called 'Brestan' and is used to control blight (*Phytophthora infestans*) in potatoes[10].

Certain organotin compounds such as tributyltin fluoride can also be incorporated into rubbers and plastics [4, 11, 12] to prevent marine fouling and also mould growth under damp conditions. Some of the disadvantages of simple incorporation of a fungicide into rubber include (i) serious retardation of the curing system; (ii) possible impairment of the physical properties of the vulcanizate; (iii) a wastefully high rate of release of the fungicide; and (iv) a limited lifetime for the material.

In order to overcome these drawbacks vulcanizates have been prepared in which the fungicide, in this case tributyltin acrylate (TBTA), is co-vulcanized into the rubber network by the use of a peroxide curing system, an approach which has been discussed in detail elsewhere[4].

The elastomers chosen were polychloroprene (CR), acrylonitrile-butadiene (nitrile; NBR) and ethylene-propylene terpolymer (EPDM) on the basis of their specific properties such as heat resistance, oil resistance and long-term ageing characteristics. All these rubbers are widely used in military equipment for toroidal sealing-ring applications[13–15]. About 5% by weight of TBTA was incorporated into the fungicidal vulcanizate. This is a higher level of fungicide than would normally be used but was selected because curing characteristics and physical properties were not impaired, long-term retention of active material was sought

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and any problems associated with the material ought then to be revealed.

3. Experimental

3.1 Assessment of performance

As extensive trials over a 15-year period in tropical Australia have shown the susceptibility of most rubbers and plastics to attack by fungi[32], it was considered essential to conduct field trials on the newly developed vulcanizate systems. In addition, our experience is that accelerated trials can be used only for general guidance and not as a guarantee of long-term practical performance under adverse conditions of service use.

Experiments were designed using two concentric O-rings to form an enclosed and sealed cavity between selected metallic and non-metallic substrate materials. With each pair of rings used to form the cavity, one contained the fungicide while the other was used as a control specimen.

This design was used to ensure that a continuous supply of fungicide was available to the cavity from the smaller O-ring. The arrangement enabled the number of specimens for the trial to be kept to a reasonable level. An important aspect of the trial was the use of low-cost, maintenance-free equipment with the minimum of instrumentation.

3.2 Elastomeric materials

The rubber formulations are shown in Table 1 and compounding ingredients in Appendix 1. Other compounding materials comparable in chemical composition and activity should be equally satisfactory. TBTA was prepared from bis(tributyltin) oxide and acrylic acid by recognized procedures[16]. The formulations were mixed on a 200 x 75 mm laboratory 2-roll mill and curing characteristics were determined on a Monsanto Model LSD rheometer. O-rings (4-cavity mould) and test sheets (2-cavity mould, 225 x 125 x 1·9 mm) were vulcanized in an electrically heated press at 160°C for 30 min. The preparation and inspection of the O-rings conformed as closely as possible to established standards[17, 18]. Mechanical properties (Table 1) of test sheets were determined under standard conditions[19, 20]. The properties of the O-rings were determined on an Instron Model 1026 tensometer using a motorized specimen-holder drive unit and standard operating conditions[21–27].

The O-rings were coded thus:

Vulcanizate	Control	Fungicidal (5%TBTA
Polychloroprene	CR-C	CR-F
Nitrile	NR-C	NR-F
Ethylene-propylene terpolymer	EP-C	EP-F

The dimensions of the rings of circular cross-section were: control (large ring), external diameter 82·6 mm, internal diameter, 72·0 mm; fungicidal, (small ring) external diameter 39·6 mm, internal diameter 28·0 mm.

3.3 Substrate materials

The ten metallic, glass and plastics materials used in the assemblies were: aluminium plate (a magnesium-aluminium alloy with good resistance to corrosion by sea-water), commercial stainless steel (for disks and hardware); nylon 11, natural; poly(methyl methacrylate) (PMMA), transparent; acrylonitrile-butadiene-styrene (ABS), white; polypropylene (PP), natural; rigid poly(vinyl chloride) (UPVC), grey; glass-reinforced polyester resin (GRP), natural; polycarbonate (PC), transparent; and glass, polished plate. Surface textures of disks were measured with a Taylor Hobson 'Talysurf' instrument[28]. The centre line average (CLA) readings were taken at eight random positions on each specimen face using an instrument cut-off of 0·8 mm and trace length of 3·8 mm. The assessment of fungicidal activity of materials used in the test assemblies was determined by standard techniques[29].

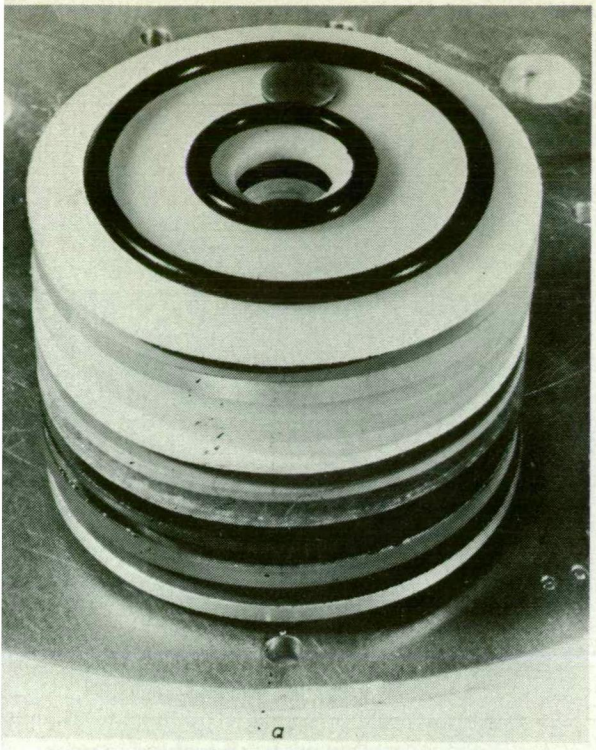
3.4 Test assemblies

Each test assembly (Fig. 1) consisted of a circular aluminium base plate 300 mm diameter x 6 mm thick, with three 20 mm-diameter holes equidistantly spaced, 55 mm from the outside edge. Three stacks of ten disks of different materials, each 100 mm diameter and with a 20mm-diameter hole at the centre, were placed so that the holes in the dis

Table 1. Rubber formulations for use in O-rings

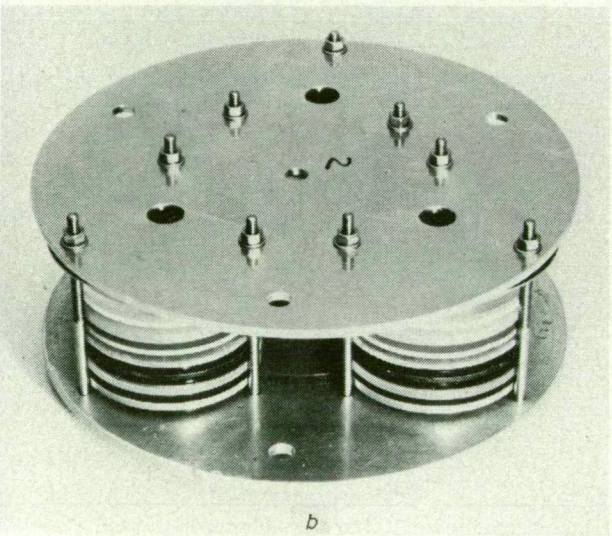
Compounding ingredients	Rubber designation					
	CR-C	CR-F	NR-C	NR-F	EP-C	EP-F
Polychloroprene (CR)	100	100				
Butadiene-acrylonitrile (NBR)			100	100		
Ethylene-propylene terpolymer (EPDM)					100	100
Carbon black	30	30	30	30	30	30
Zinc mercaptobenzimidazole			2	2	2	2
Diaryl-*p*-phenylenediamine	2	2				
Stearic acid	1	1				
Zinc oxide	5	5				
Magnesium oxide	4	4				
2-Mercaptoimidazoline	1	1				
Dicumyl peroxide		3	3	3	3	3
Trimethylol propane trimethacrylate		3	3	3	3	3
Tributyltin acrylate		8		7		7
	Original properties[(a)]					
Tensile strength, MPa	19.2	15.1	19.4	19.2	14.7	15.4
Elongation at break, %	270	200	340	300	700	640
Hardness, IRHD	68	70	54	55	44	45
Compression set, 24 h at 70°C, %	13	15	12	11	24	23
Cold flex temperature, °C[(b)]	–32.5	–36.5	–22.5	–23.5	–63	–65

(*a*) Determined on moulded test sheets.
(*b*) B.S. 2571–1963 (Clash and Berg method).



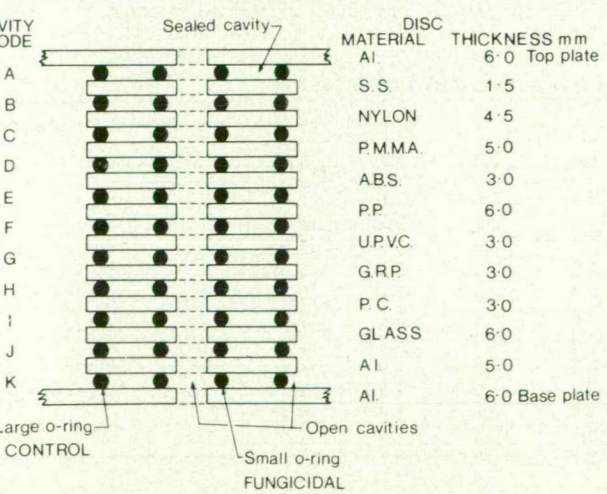
a

. 1a Typical stack during assembly (CR-C, CR-F)



b

. 1b Complete assembly (control)



. 2 Sequence of materials used in each stack in each test embly

were collinear. Between each pair of surfaces, one large control 0-ring and one small fungicidal 0-ring of the same base rubber were placed concentrically to form an annular cavity sealed by the two rings. Two 0-rings were placed similarly on the top of each stack, and a top plate, similar to the base plate, was added. Each assembly was held together with nine stainless-steel bolts. The combinations of 0-rings in each of the three stacks per test assembly were CR-C and CR-F, NR-C and NR-F and EP-C and EP-F. The sequence of materials in the assembly is shown in Fig. 2.

During assembly a small disc of nylon 6 (10 mm diameter x 2 mm thick), previously dried in a vacuum oven for 24 h at 100°C, was placed in each cavity, in order to monitor uptake of moisture. Hardness of the disc was determined[30] using the Barcol Model GYZ-J935 impressor. Each assembly was bolted together, under load, to 85% of the original thickness (15% compression).

3.5 Environmental exposure

One complete assembly and a number of unused 0-rings was stored, in the dark, at Maribyrnong, Victoria. One assembly was exposed outdoors at Maribyrnong and another outdoors at JTRU, Innisfail, Queensland ('hot-wet' tropical) at a cleared site near the jungle. These assemblies were exposed in a horizontal position, about 1 m above the ground and were protected from direct solar radiation by a 400 mm diameter opaque plastics sheet fixed 25 mm above the assembly.

A fourth assembly was submerged in a tank of flowing seawater at Naval Dockyard, Williamstown, Victoria. The assemblies were exposed for 3 yr at each site. Typical meteorological data for a 5 yr period are given in Table 2.

Table 2. Meteorological data for the five year period, 1970–74

Property	Melbourne, Vic. (temperate)	Innisfail, Qld. (hot-wet, open)
Latitude, S	37° 49′	17° 32′
Longitude, E	144° 58′	145° 58′
Elevation, m	34.7	39.6
Temperature, °C (Average daily max)	20	28
Relative humidity, % (Average index)	55	82
Total rainfall, mm	3597	18145
Total sun, h	11406	11723

With six different rubbers (3 control, 3 fungicidal), ten different materials, two types of cavities (open and closed) and four environmental exposure conditions, the number of variables totalled 480.

3.6 Assessment

Assemblies returned from exposure and controls were examined for any cracking of rings and for the presence of fungal growth. On dismantling, adhesion between rings and substrates was assessed and the hardness of each small nylon indicator disc measured. The axial and radial thicknesses of each ring were measured 0·5 h, 24 h and 48 h after dismantling. Hardness of rings was measured[31] after 24 h and tensile properties after 48 h. Substrate materials were examined for signs of stress cracking and corrosion and annular cavities for signs of fungal growth or changes in transparency of particular materials. Residual fungicidal activity of rings was assessed[43].

4 Results and discussion

4.1 General

In order to perform satisfactorily in a sealing device, rubbers must remain stable over long periods under static stress and adverse conditions such as high and low temperatures, vibration, shock, sunlight and ozone and in the presence of a wide range of chemicals such as water, fuels, lubricants, solvents and hydraulic fluids. Mechanical properties, particularly compression set and hardness, should remain stable in order to ensure long-term sealing efficiency. In optical devices rubbers must not generate volatile chemical compounds likely to sublime onto glass components and cause loss of transparency. When equipment has to be dismantled for modificaiton or servicing, adhesive strength between rubber and substrate should be weak. All these factors were assessed as part of the trial.

The concept we have developed involves the use of high quality, peroxide-cured rubbers known to be suitable for use in military applications and the replacement of conventional monomeric, low molecular weight fungicides by high-molecular-weight active organotin compounds covulcanized into the rubber network.

4.2 Visual examination

Rings in the indoor control assembly showed no evidence of ozone cracking or deterioration. A slight texturing of the surface of the rubbers in contact with glass reinforced plastics (GRP) was evident in all assemblies.

At the temperate site, the large nitrile rings, as expected, showed extensive ozone cracking on the exposed circumference. There was no cracking of the small fungicidal nitrile ring or the polychloroprene or ethylene-propylene terpolymer rings. Rubbers exposed in assemblies in the tropics gave similar results and this is in agreement with published data[32]. All assemblies exposed outdoors showed severe contamination by dirt and other debris.

On dismantling the assemblies the adhesive strength between rings and substrates was assessed. No marked differences were evident between control and fungicidal rings in any of the assemblies and all rubbers had very weak bonds to nylon and to polypropylene.

For assemblies not immersed in seawater polychloroprene rubber showed strong bonding to both plate glass and GRP and weak bonding to ABS. Nitrile rubber showed strong bonding to GRP and UPVC, and ethylene-propylene terpolymer displayed strong bonding to GRP and to polycarbonate. For the assembly immersed in seawater, the o strong bonds identified were between all rubbers and sta less steel (probably accentuated by the presence of corrosi products), nitrile rubber to ABS and GRP and ethyle propylene rubber to ABS and UPVC.

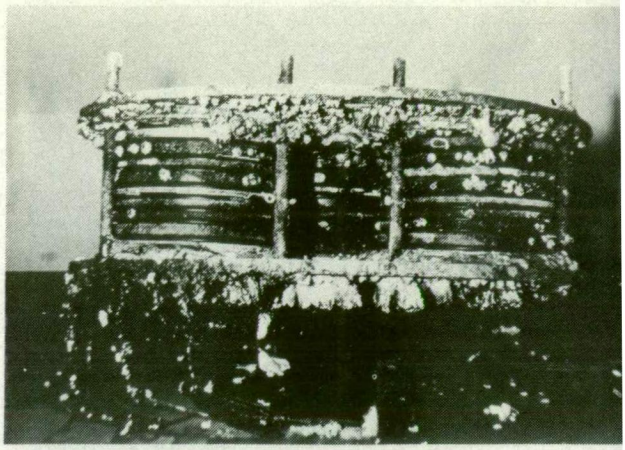


Fig. 3 Assembly after immersion in sea water for 3 years

The assembly immersed in seawater for 3 yr was heav encrusted with barnacles and other marine fouling organis (Fig. 3). The annular cavities between the aluminium co plates and the metal discs in each stack were filled with white crystalline corrosion product, identified as main aluminium salts. The rubber rings forming these cavit were slightly swollen and, in some cases, deformed. The was severe corrosion of the cover plates (Fig. 4) where th had been in contact with the rings, mainly due to crevi corrosion[33].

All rings in contact with glass and plastics were in go condition, and the sealed cavities were clean and dry. So minor hairline cracking was present on the control nitr rings.

There were no signs of stress cracking or crazing on a of the plastic materials. This is significant for polycarbona and PMMA and indicates that all of the rubbers can be us under stress, in contact with these transparent materials f long periods.

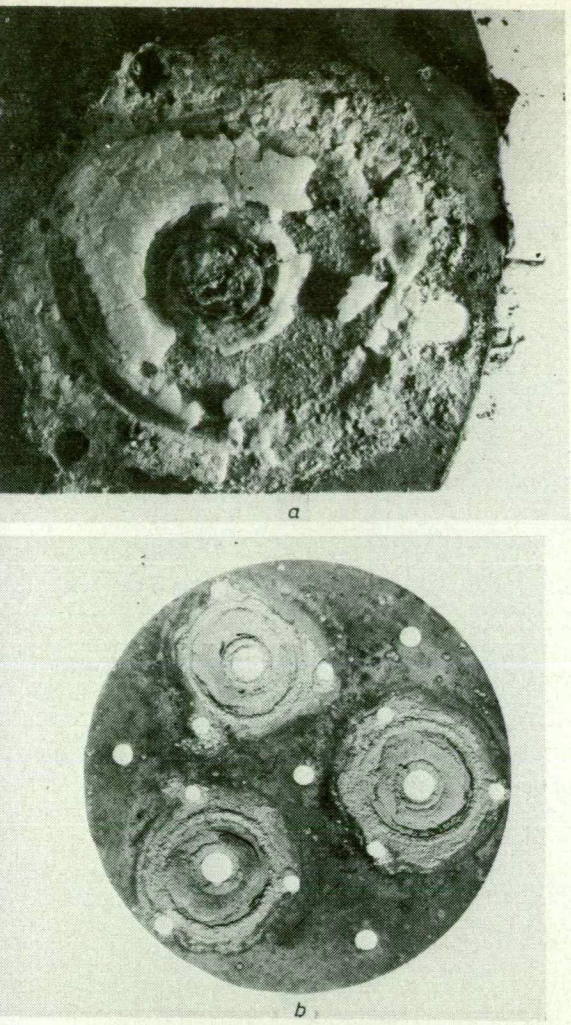
4.3 Sealing efficiency

It has been shown[34] that the indentation hardness (Barc of sheets of nylon 6 is dependent on the water content. F a sheet of specific thickness, a calibration graph as shown

Table 3. Water content (%, w/w) of nylon indicator disks after storage for 3 yr

Cavity designation[a]	Control			Temperate			Tropical			Marine immersion		
	CR[b]	NR	EP	CR	NR	EP	CR	NR	EP	CR	NR	E
A (Top)	1.8	1.8	2.2	2.1	2.9	2.5	2.8	1.6	2.5	(c)	(c)	(
B	1.4	2.2	1.8	1.4	2.4	1.6	2.6	2.8	2.8	3.4	4.2	4
C	1.6	2.1	2.1	1.6	2.4	2.1	2.8	2.9	2.9	3.3	4.5	3
D	1.8	2.1	2.1	1.8	2.6	2.6	2.8	2.2	2.6	3.7	5.1	4
E	2.0	2.0	2.1	1.8	2.8	2.4	2.6	2.0	2.4	4.0	5.1	4
F	1.8	2.1	2.1	1.7	2.6	2.4	2.9	2.0	2.5	3.4	5.3	4
G	1.8	2.0	2.2	1.8	2.5	2.4	2.9	2.1	2.9	3.7	5.1	4
H	2.0	2.1	2.2	2.1	2.4	2.6	2.8	1.8	2.5	4.0	5.3	5
I	1.8	2.0	2.1	2.0	2.4	2.5	2.9	1.7	2.4	4.0	5.1	4
J	1.8	2.1	2.1	2.1	2.9	2.4	2.9	1.4	2.4	(c)	(c)	(
K (Base)	2.1	2.1	2.0	2.1	2.6	2.4	2.4	1.4	2.4	(c)	(c)	(

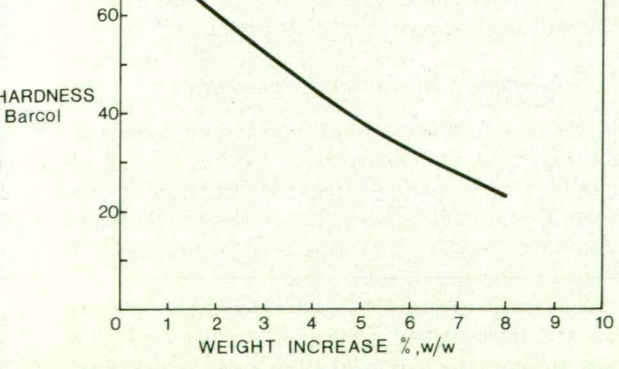
(a) See Fig. 2.
(b) Annular cavity sealed by type of rubber as designated. Thus CR (polychloroprene) cavity formed by CR-C large ring and CR-F small ri
(c) Not applicable owing to corrosion products in the cavity.



ig. 4 Aluminium baseplate showing the effects of crevice cor-osion
Before cleaning
After cleaning

Fig. 5 can be constructed to relate hardness and water content. By placing an indicator disc of nylon, dried to zero water content, in each sealed cavity and measuring the hardness of the disc when the assembly was dismantled, an indication of moisture content of the nylon was obtained.

Dried indicator discs were exposed to relative humidities of 0%, 30%, 52% and 100% at 23°C and also to a laboratory



ig. 5 Relation between Barcol hardness of nylon indicator disks nd water content determined by weight increase

atmosphere without humidity control at the same temperature during the dry summer period. The percentage weight increase of the discs is plotted against the time of exposure in Fig. 6. The water content of each indicator disc in the trial, derived from the measured hardness and the calibration graph, Fig. 5, is shown in Table 3.

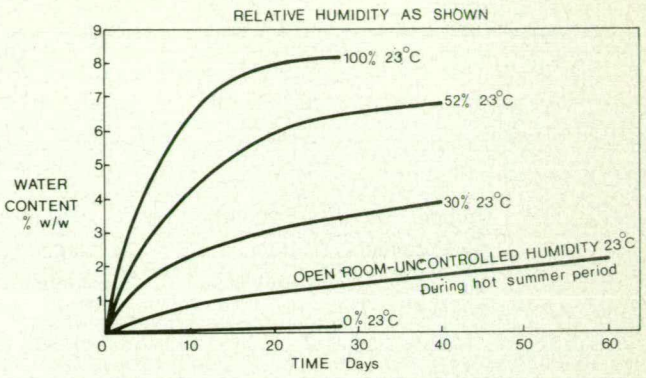


Fig. 6 Water uptake of nylon indicator disks

The water content of indicator discs in the control assembly was about 2% and for assemblies exposed under temperate and tropical conditions it was always less than 3%, suggesting good sealing efficiency. As expected, higher equilibrium water contents were found in discs from the assembly immersed in seawater – the maximum result was 5·3%. Cavities sealed with polychloroprene and ethylene-propylene rubbers had lower moisture contents than those sealed with nitrile rubbers.

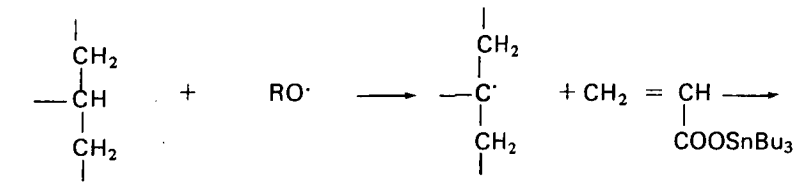
As the average water content of indicator discs in the control assembly was about 2%, and from Fig. 6 discs exposed under ambient conditions gain about 2% moisture in 50 days, the sealing obviously has a marked effect on the rate of diffusion of moisture into the cavities over the 3 yr trial period. The absorption of water by elastomers has been studied[35, 36] and the equilibrium water absorption by gum vulcanizates at 88% r.h. was estimated as 0·75% for SBR, 0·5% for natural rubber and 0·25% for butyl rubber. By contrast, polychloroprene rubbers continued to absorb water because of the metal oxide curing system, a value of 1·9% being reported after 2 d. In the present case we are concerned with the transmission of moisture through a compressed rubber ring, and it appears that the three rubbers give similar performance.

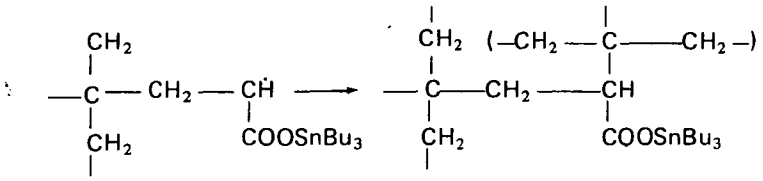
The average relative humidity for the temperate and for the tropical sites is 55% and 82% respectively (Table 2). Under these conditions the equilibrium moisture value for the indicator disc is about 7% and 8% respectively (Fig. 6). As indicator discs after 3 yr in trial assemblies had moisture values much less than equilibrium value for discs with free access to moisture, effective sealing must have been maintained.

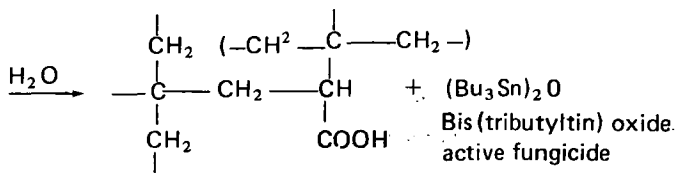
For the assembly immersed in sea water one side of each ring was exposed to water for 3 yr, and the average moisture content of indicator discs was about 5% (excluding metal-metal cavities subjected to crevice corrosion). In the long term, a relative humidity of 30% or less would produce a similar equilibrium value. This indicates that the average humidity in the sealed cavities under marine immersion conditions was substantially less than 50%.

4.4 *Antifungal performance*

Rubbers containing covulcanized TBTA are designed to slowly release an organotin compound known to be toxic to most fungi usually found in tropical areas. As shown previously[4], although the organotin groups are firmly bound into the rubber network, when water diffuses into the rubber reactions occur which cause the release of fungicidally active compounds as shown below:







This process is known to be slow and ensures that active material is not rapidly depleted from the rubber. When cavities are first sealed by the use of covulcanized 0-rings, any low molecular weight residual organotin fungicide will volatilize and give immediate short-term protection. Ingress of any moisture will initiate hydrolysis of active organotin groups and release bis(tributyltin) oxide into the cavity. In the absence of moisture no change in the organotin polymer will occur.

No fungal contamination was observed inside any sealed cavity of the assemblies (Fig. 7). The assembly from the tropical area which would have been most susceptible to fungal attack had slight fungal growth present on the outer exposed surfaces of the control rings, but none on or near the inner fungicidal rings. Microscopic examination of a the materials inside the sealed cavities failed to show th presence of any micro-organisms. All the small fungicid rings including those immersed in sea-water for 3 yr, we found to be fungicidally active at the end of the 3 yr tri period. This confirms the long-term nature of the fungicid performance of these vulcanizates.

It has been reported that to promote adequate sealing surface finish better than 0·8 μm Ra is desirable[37]. Table indicates that, with the exception of one side of the stai less steel and glass reinforced plastics discs, all substrat conformed to the recommended finish. The adequate finis of the substrates combined with the durability of the rub ber 0-rings and the plastics materials all contributed t sealing efficiency and lack of fungal growth inside seale cavities.

Table 4. Surface texture of disks

Material	Surface texture[a]	
	Side 1	Side 2
	μm Ra	μm Ra
Aluminium	0·3	0·2
Stainless steel	0·4	1·9
Nylon 11	0·6	0·6
Poly(methyl methacrylate)	0·1	0·1
Acrylonitrile-butadiene-styrene	0·05	0·2
Polypropylene	0·7	0·2
Rigid poly (vinyl chloride)	0·6	0·8
Glass-reinforced polyester	0·9	0·8
Polycarbonate	0·2	0·3
Glass	0·005	0·005

(a) Centre Line Average (CLA) readings.

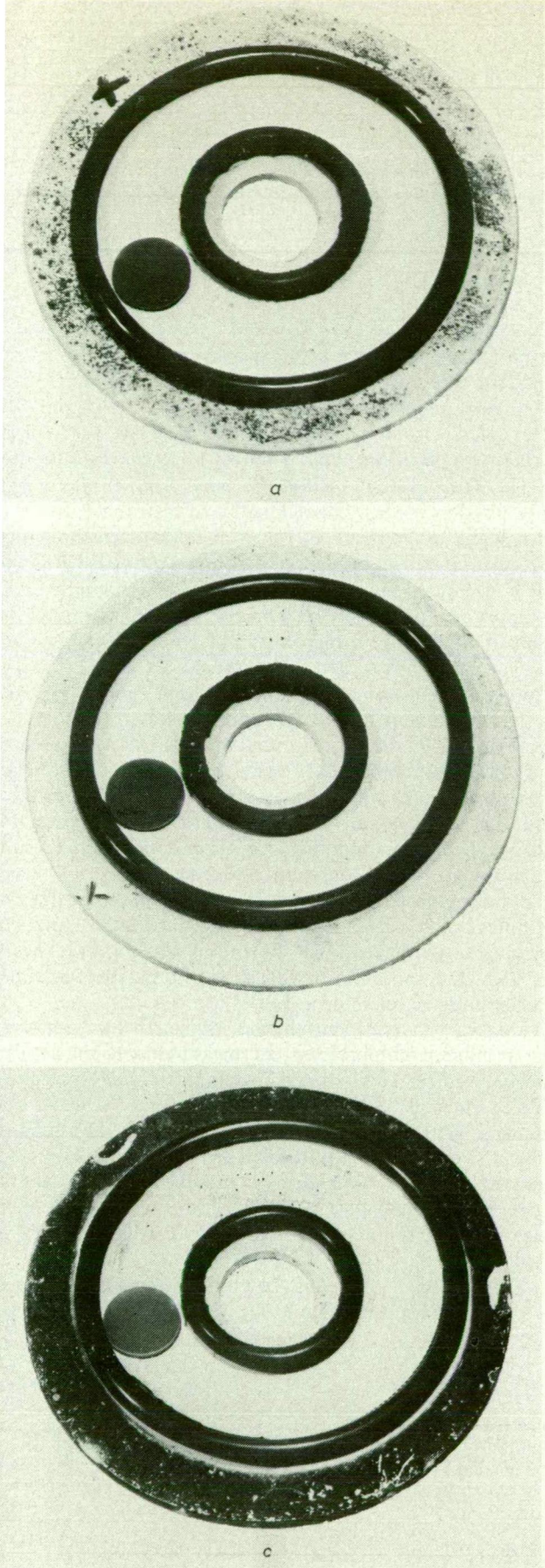
For cavities containing transparent substrate materia there was no evidence of condensation of fungicide o any internal surface and no loss of transparency. This particularly significant if optical devices are to be protecte from fungal attack.

As sealed cavities made by the combination of 0-ring and planar surfaces can be protected by the use of covulca nized fungicides, it is predicted that the use of similar ring located in traditional grooves will be even more effectiv in preventing ingress of fungal growths.

4.5 *Assessment of mechanical properties*

Meyers and Wenrick[38] have reported on the effect of tes piece geometry on mechanical properties. The results of ou investigation comparing 0-rings and test pieces from standar sheets are given in Table 5. This enables a relationship to b established between materials used in long-term trials an original properties of vulcanizates.

The effect of size of 0-rings (some specially moulded was also investigated (Table 6). In all cases the tensil strength measured on large rings was greater than that o the same rubber measured on small rings. For the sam



ig. 7 Sealed cavities on dismantling after 3 years exposure show-
g absence of fungal growth and location of nylon indicator disks
Temperate, rubber NR-C, NR-F, cavity D, ABS
Tropical, rubber NR-C, NR-F, cavity D, ABS
Marine immersion, rubber NR-C, NR-F, cavity D, ABS

Table 5. Comparison of dumb-bell and O-ring test specimens

Rubber designation	Tensile strength		Elongation at break	
	Dumb-bell[a]	O-ring[b]	Dumb-bell[a]	O-ring[b]
	MPa	MPa	%	%
CR-C	19·2	17·3	270	270
CR-F	15·1	12·9	200	217
NR-C	19·4	16·4	340	330
NR-F	19.2	13.5	300	360
EP-C	14.7	13.6	700	840
EP-F	15·4	13·5	640	700

(*a*) Determined at time of moulding.
(*b*) Determined after indoor storage, unstressed, for 3 yr.

Table 6. Effect of ring size on mechanical properties

Rubber designation	Internal diameter[a]	Tensile strength	Elongation at break	Hardness
	mm	MPa	%	IRHD
CR-C[b]	28	7·8	200	70
CR-C	72	17·3	270	70
CR-F	28	12·9	220	73
NR-C[b]	28	12·9	320	60
NR-C	71	16·4	330	59
NR-F	28	13·5	360	58
EP-C[b]	28	12·0	850	51
EP-C	71	13·6	840	52
EP-F	28	13·5	700	54

(*a*) The axial and radial thickness of all rings varied within the limits 4·6 to 4·9 mm.
(*b*) Specially moulded for this evaluation.

rings, rubbers containing organotin fungicide had higher tensile strengths than control rubbers.

The excellent performance of the peroxide curing system to accelerated ageing in air and in water is confirmed by the results given in Table 7.

4.6 Trial results: mechanical properties

The tensile strength, elongation at break and compression set results for 0-rings used in the trial are given in Figs. 8, 9 and 10 respectively. In Figs. 8 and 9, 'original' indicates unstressed rings, stored unassembled in the dark at 23°C. All other results are rings removed from assemblies.

Properties of unstressed rings and those held under compression in the control assembly were similar for each rubber. In confirmation of accelerated ageing results, the fungicidal polychloroprene rubber, CR-F, showed major changes in properties as a result of water immersion. This is not unexpected for this polymer.

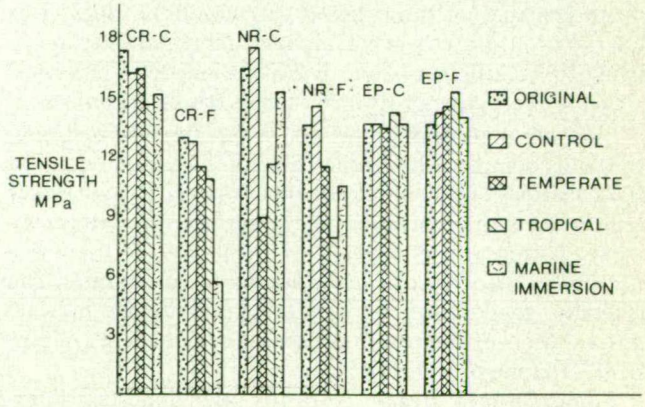


Fig. 8 Tensile strength of 0-rings after 3-year exposure

Table 7. Accelerated ageing of O-rings

Rubber designation	Tensile strength			Elongation at break		
	Original	Air, 7 days at 70°C	Water, 7 days at 70°C	Original	Air, 7 days at 70°C	Water, 7 day at 70°C
	MPa	MPa	MPa	%	%	%
CR-C(a)	17.3	17.2	15.2	270	270	240
CR-F(b)	12.9	14 8	10.8	220	250	180
NR-C(a)	16·4	18·6	17·6	330	380	380
NR-F(b)	13·5	13·9	8.3	360	320	280
EP-C(a)	13·6	12·8	12·8	840	890	880

(a) Large O-rings, internal diameter 72 mm
(b) Small O-rings, internal diameter 28 mm

All the large rings (CR-C, NR-C and EP-C) were more liable to attack by ozone and to deterioration by sunlight than the small rings. The lower tensile strength values observed for the nitrile rings at the temperate and tropical sites, compared with original values, reflect the effect of

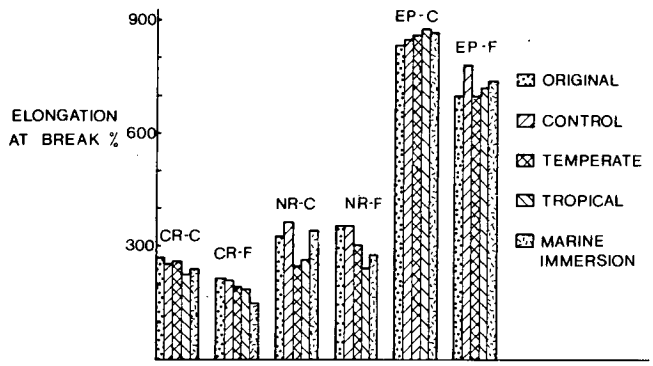


Fig. 9 Elongation at break of O-rings after 3-year exposure

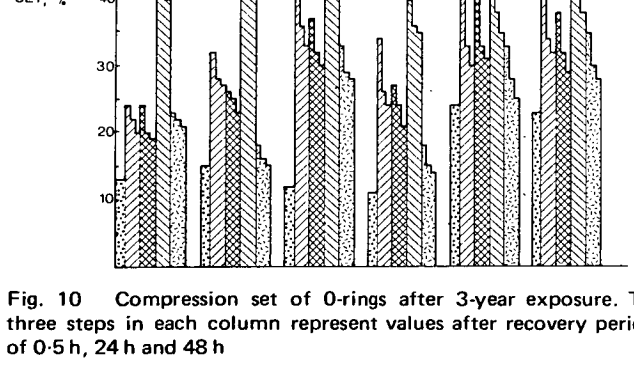


Fig. 10 Compression set of O-rings after 3-year exposure. The three steps in each column represent values after recovery periods of 0·5 h, 24 h and 48 h

ozone cracking on the exposed surface of the rings. This deterioration did not occur in rings immersed in seawater owing to exclusion of ozone. Excellent long-term resistance to ageing of ethylene-propylene rubbers has been confirmed.

Elongation at break properties, in general, followed similar trends compared to tensile strength. The good retention of elongation at break of nitrile rubbers immersed in seawater again reflects the protection of the surface from attack by ozone. Changes in elongation at break can be used as a measure of the extent of deterioration of vulcanizates. The generally good values for the fungicidal O-rings indicate that addition of tributyltin acrylate is not in any way detrimental to long-term performance.

Compression set results (Fig. 10) offer important information on longterm sealing characteristics. The "original" results were obtained by conventional methods[39] from standard compression set test pieces, evaluated at 70°C for 24 h. Measurements on rings were made 0·5 h, 24 h and 48 h after release from the assembly and were averaged for all O-rings of a particular type of rubber for each exposure site.

The drop in compression set value from 0·5 h to 24 h indicates the recovery characteristics of the rubber. Rubbers with high compression set values at 0·5 h often show high recovery rates. The two polychloroprene rubbers, CR-C and CR-F, exhibited good compression set results despite being compressed 15% for 3 yr. For the control assembly the value for CR-C (48 h recovery) was 20%. The presence of covulcanized TBTA had little effect on overall results. However, compression set values for both rubbers exposed in the tropics were higher than at other sites.

With nitrile rubber, the presence of TBTA resulted in improved compression set characteristics. The difference between the short-term conventional compression set value and that of the control O-ring assembly was greater for nitrile rubber than for polychloroprene. Conventional results do not relate well to long-term performance.

Ethylene-propylene terpolymers showed large values of compression set after 0.5 h recovery but these reduced to levels close to conventional short-term values after recovery for 48 h. Incorporation of TBTA had no deleterious effect on compression set value in EPDM rubbers.

Moakes[40, 41] and Morrell and Watson[42] have reported the results of compression set measurements on annular specimens after 15 yr storage in temperate and tropical (at JTRU, Innisfail) areas. They concluded that "it seems that standard type compression set tests in which the rubber is only compressed for up to 24 h, are inadequate to predict behaviour under long-term compression". Our results agree with this conclusion and confirm that all the rubbers used in our trials should be suitable for use in longterm sealing applications.

None of the O-rings showed marked changes in hardness as a result of exposure (Table 8).

Table 8. Hardness changes during exposure

Rubber designation	Original hardness	Mean change in hardness			
		Control	Temperate	Tropical	Marine immersio
	IRHD	%	%	%	%
CR-C	70	+1·4	+1·4	+2·9	0
CR-F	73	0	0	−1·4	−5·5
NR-C	59	0	−1·7	+1·7	−5·1
NR-F	58	0	−1·7	+5·2	−3·4
EP-C	52	+1·9	0	+1·9	−3·8
EP-F	54	0	0	+3·7	−1·9

Conclusions

he performance of elastomeric 0-rings produced from ıree different synthetic rubbers containing covulcanized ributyltin acrylate as a long-lasting fungicide, has been ssessed in the laboratory and in field trials, over 3 yr. Sealed avities formed between the 0-rings and glass, seven different lastics, stainless steel and aluminium remained dry and ee from microbiological growth during exposure to several dverse environments. The fungicidal activity of the vulcaizates was found to be retained during the 3 yr trial period.

The long-term compression set of the 0-rings was greater ıan predicted from conventional short-term tests at elevated emperature. Other mechanical properties were not greatly ffected by the trial exposures under 15% compression. 'ertain combinations of elastomers and plastics would not e recommended for applications where ease of separation after long periods of compression was important. The elastomers did not promote stress cracking in any of the plastics and optical properties of transparent materials were unchanged. The incorporation of the organotin fungicides into the rubbers effectively prevented fungal contamination of the 0-rings and adjacent areas. This technique can be used with most hydrocarbon rubbers.

Acknowledgements

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eferences

. UPSHER, F. J. (1976) Microbial Attack on Materials. *Proc. Roy. Aust. Chem. Inst.*, 43, 173
. BLACKLEY, D. C., TUPPER, D. C. and YARD, J. O. (1958) Ageing of Natural Rubber Mixes Containing Various Fungicidal Bactericidal Additives. Report No. B/109 (R). Admiralty Materials Laboratory, Holten Heath, Poole, Britain
. OLDFIELD, D. (1973) Organotins in Polymer Chemistry. *Proc. Roy. Aust. Chem. Inst.*, 40, 23
. DUNN, P. and OLDFIELD, D. (1975) *Rubb. Ind.*, 9, (1), 34
. BLOW, C. M. (1972) Rev. Bibliog. Aspects of Fluid Sealing, p. 41. British Hydromechanical Research Association
. BLOW, C.M. and LAWRIE, J. M. (1973/74). *Prog. Rubb. Technol.*, 37, 41
. (1972) Contamination Control Technology. MIL-HDBK-408, Department of Defence, United States of America.
. (1970) Solid Rubber Seals and Joints, Tech. Rev. 53. Rubber and Plastics Research Association, Shawbury, Shropshire, Britain.
ALLEN, R. E. (1969) 0-Rings Make History. Otterbein, Dayton, Ohio
0. LUIJTEN, J. G. A. (1972) (Ed. A. K. SAWYER) *In* Organotin compounds, p. 940. Marcel Dekker New York
1. DUNN, P. (1962) Elastomeric and Fungicidal Organotin Compounds. Paper presented at 36th Congress ANZAAS, Sydney. Defence Standards Laboratories, Department of Supply
2. WOODFORD, J. M. D. (1972) Underwater Marine Coatings. Part II: Marine Biocidal Rubbers Containing Organotin Toxics. M.R.L. Report 496
3. (1963) Vulcanized Polychloroprene Rubbers for Aircraft. Specification DTD 5514A. Aerospace Materials Specification. Ministry of Technology, Britain.
4. (1970) Elastomeric Toroidal Sealing Rings. Butadiene-Acrylonitrile Type (Mineral Oil Resistant). Specification DTD 5606. Aerospace Materials Specification, Ministry of Technology, Britain.
5. (1970). Elastomeric Toroidal Sealing Rings. Fluid Resistant Vulcanized Ethylene–Propylene Type. Specification DTD 5608. Aerospace Materials Specification, Ministry of Technology, Britain.
6. MONTERMOSO, J. C., ANDREWS, T. M. and MARINELLI, L. P. (1958) *J. Polym. Sci.*, 32, 523.
7. (1968) Elastomeric Toroidal Sealing Rings (0-Rings). Manufacturing and Inspection Standards for Aerospace Applications. Technical Specification No. 49. The Society of British Aerospace Companies Ltd., Britain
8. (1972) Inch Dimensions of Toroidal Sealing Rings and their Housings (0-Rings). Specification AS-B320. Standards Association of Australia, Sydney
19. (1971) Determination of Tensile Stress-Strain Properties. BS 903: Part A2. British Standards Institution, London
20. (1968). International Hardness of Vulcanized Rubber, ASTM D1415-68. American Society for Testing and Materials, Philadelphia, Pa.
21. (1972) Standard Methods of Testing Rubber 0-Rings. ASTM D1414–72. American Society for Testing and Mateirals, Philadelphia, Pa.
22. (1974) 0-Ring Standard Dimensional Measurement Practices. Technical Bulletin, Rubber Manufacturers Association, Washington
23. (1974) 0-Ring Dual Dimensional Size Standard. Technical Bulletin, Rubber Manufacturers Association, Washington
24. (1974) 0-Ring Hardness; Comparison of Test Methods. Technical Bulletin, Rubber Manufacturers Association, Washington
25. (1974) Compression Set and its Relationship to 0-Ring Performance. Technical Bulletin, Rubber Manufacturers Association, Washington
26. (1970) Test Methods for 0-Ring Compression Set in Fluids. Technical Bulletin, Rubber Manufacturers Association, Washington
27. (1969) 0-Ring Corrosion Standard. Technical Bulletin, Rubber Manufacturers Association, Washington
28. (1962) Centre-Line Average Height Method (M-System) for the Assessment of Surface Texture. Specification AS-B131. Standards Association of Australia, Sydney
29. (1972) Method of Testing Materials for Resistance to Fungal Growth. Part II: Rubbers and Plastics. Specification AS-1157. Standards Association of Australia, Sydney
30. (1967) Indentation Hardness of Plastics by Means of a Barcol Impressor. ASTM D2583 (reapproved 1972). American Society for Testing and Materials, Philadelphia, Pa
31. BROWN, R. P. and HUGHES, R. C. (1972) *RAPRA Bull.*, 26, (7), 183
32. DUNN, P. and HART, S. J. (1969) *IRI J.*, 3, (2), 1.
33. GODARD, H. P., JEPSON, W. P., BOTHWELL, M. R. and KANE, R. L. (1967) The Corrosion of Light Metals, P. 45. Wiley New York
34. DUNN, P., LIGGINS, T. and NORRIS, T. (1967) Case and Seal Materials for Telephone Set K. Part I. D.S.L. Report 300
35. DERHAM, C. J. (1972) Proc. Int. Rubb. Conf. Fl. Institution of the Rubber Industry, London
36. BRIGGS, G. J., EDWARDS, D. C. and STONEY, E. B. (1962) Proc. 4th Rubb. Technol. Cong., p. 362. Institution of the Rubber Industry, London.
37. (1970) Parker 0-Ring Handbook. Parker Seal Company, Culver City, Calif.
38. MEYERS, F. S. and WENRICK, J. D. (1974) *Rubb. Chem. Technol.*, 47, 1213.

39. (1969) Compression Set of Vulcanized Rubber. ASTM D395-69. Method B, Type 2. American Society for Testing and Materials, Philadelphia, Pa.
40. MOAKES, R. C. W. (1975) RAPRA Members J. (Sept./Oct.), 77. Rubber and Plastics Research Association, Shawbury, Britain
41. MOAKES, R. C. W. and NORMAN, R. H. (1977) Long Term Natural Ageing. Paper presented at Conference on Techniques for Assessing the Environmental Behaviour of Non-Metallic Materials. Society of Environmental Engineers, Materia Group. Imperial College of Science and Technology, Londo Paper 5, 27 April
42. MORRELL, S. H. and WATSON, W. F. (1976) RAPRA Mer bers J. (May/June), 59. Rubber and Plastics Research Associ tion, Shawbury, Britain
43. (1963) Determining Resistance of Plastics to Fungi,ASTM 1924-63. American Society for Testing and Materials, Phil delphia, Pa.

APPENDIX 1
Materials

	Trade name	Supplier
1. Compounding materials		
Bis (tributyltin) oxide	TBTO	Osta Chemicals Ltd.
Butadiene-acrylonitrile rubber	Butakon A3003	ICI Aust. Ltd.
Carbon black	Acarb 600	Australian Carbon Black Pty. Ltd
Diaryl-*p*-phenylenediamine	Akroflex AZ	Du Pont Inc.
Dicumyl peroxide (40% active)	Dicup 40C	Hercules Powder Co.
Ethylene-propylene terpolymer	Nordel 1440	Du Pont Inc.
2-Mercaptoimidazoline	NA-22	Du Pont Inc.
Polychloroprene rubber	Neoprene WRT	Du Pont Inc.
Trimethylolpropane trimethacrylate	SR 350	Sartomer Resin Inc.
Zinc mercaptobenzimidazole	ZMB	Bayer Australia Ltd.
2. Substrate materials		
Acrylonitrile-butadiene-styrene	Cycolac	Marbon Chemicals Ltd.
Aluminium	Alloy M57S--H34	Australuco Aluminium Co.
Glass	Polished plate	Commercial supplier
Glass-reinforced polyester	GRP	Melbourne Fibreglass Panels
Nylon 11	Rilsan	Cadillac Plastics (Aust.) Pty Ltd.
Polycarbonate	Lexan	General Electric Co.
Poly (methyl methacrylate)	Perspex	ICI Aust. Ltd.
Polypropylene	Polypropylene	Shell Chemical (Aust.) Pty. Ltd.
Rigid poly (vinyl chloride)	Darvic	ICI Aust. Ltd.
Stainless steel	Style 18/8	Commercial supplier

APPENDIX 14 ORGANOTINS AS FUNGICIDES FOR PLASTICISED POLY(VINYL CHLORIDE)

14a Fungicides for Use with Poly(Vinyl Chloride)
P. DUNN and E.J. HILL
Report 298. Defence Standards Laboratories, Department of Supply, Melbourne, Australia. 14.2 - 14.4

14b Properties of Weathered Poly(Vinyl Chloride)
P. DUNN and E.J. HILL
Report 410. Defence Standards Laboratories, Department of Supply, Melbourne, Australia. 14.5 - 14.6

14c Weathering of Plasticised Poly(Vinyl Chloride)
P. DUNN, D. OLDFIELD and R.H. STACEWICZ
J. Appl. Polym. Sci., 14, 2107 (1970) 14.7 - 14.16

14d Weathering of Improved Plasticised Poly(Vinyl Chloride).
P. DUNN, D. OLDFIELD and G.F. SANSOM
Paper D5. *International Symposium on the Weathering of Plastics and Rubbers*. The Plastics and Rubber Institute, London, Britain. 8-9 June, 1976. 14.17 - 14.30

The work presented at Appendix 14d is an unabridged retype from the grid sheets used to produce the original preprints for the symposium.

DEPARTMENT OF SUPPLY
AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
DEFENCE STANDARDS LABORATORIES

REPORT 298

FUNGICIDES FOR USE WITH POLYVINYLCHLORIDE

P. DUNN and E. J. HILL

SUMMARY

Flexible polyvinylchloride compounds containing fungus-susceptible plasticizers and selected fungicides have been exposed under tropical "hot-wet", tropical "hot-dry" (desert) and temperate conditions. Nine organotin fungicides and nine commercial organic fungicides have been evaluated in these compounds at two concentrations. Two ultraviolet absorbers have also been investigated as stabilizers for polyvinylchloride compounds containing selected organotin fungicides.

Both organotin and organic fungicides lost much of their fungicidal activity after exposure for 18 months. The incorporation of fungicides did not retard deterioration of polyvinylchloride compounds on exposure. The use of ultraviolet absorbers in conjunction with organotin compounds resulted in the retention of some fungicidal activity after exposure. By the use of selected plasticizers flexible polyvinylchloride compounds that retain good physical properties after exposure can be obtained.

SEPTEMBER, 1967

POSTAL ADDRESS Chief Superintendent, Defence Standards Laboratories, Box 50, P.O., Ascot Vale, Victoria, 3032

PRINTED BY DEPARTMENT OF SUPPLY, CENTRAL DRAWING OFFICE, MARIBYRNONG, 3032

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DEPARTMENT OF SUPPLY
AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
DEFENCE STANDARDS LABORATORIES

REPORT 410

PROPERTIES OF WEATHERED POLY(VINYL CHLORIDE)

P. DUNN and E. J. HILL

SUMMARY

In order to evaluate the resistance of plasticized poly(vinyl chloride) (PVC) to weathering, a series of compounds containing different organotin additives and ultraviolet absorbers has been exposed outdoors for up to 5 years at four sites in Australia with widely differing climatic conditions.

Following exposure, the mechanical properties of the poly(vinyl chloride) compositions were determined. It has been shown that, with the exception of elongation at break, assessment of weathering of this type of plastic using standard mechanical tests does not give a satisfactory indication of overall performance. Visual examination of the specimens, determination of elongation at break and measurement of changes in the chemical and physical properties of the base polymer appear to be more realistic methods for assessing the degradation of PVC due to weathering.

OCTOBER, 1970

POSTAL ADDRESS: Chief Superintendent, Defence Standards Laboratories, Box 50, P.O., Ascot Vale, Victoria 3032.

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Table 9 - Effect of additives on elongation at break

* * * *

JOURNAL OF APPLIED POLYMER SCIENCE VOL. 14, PP. 2107–2116 (1970)

Weathering of Plasticized Poly(vinyl Chloride)

P. DUNN, D. OLDFIELD, and R. H. STACEWICZ, *Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, Melbourne, Australia*

Synopsis

A series of flexible plasticized poly(vinyl chloride) (PVC) compositions containing different organotin compounds and ultraviolet absorbers has been exposed for 4.5 years at four outdoor sites in Australia with widely differing climatic conditions. Loss of plasticizer by evaporation during the exposure was measured and an empirical correlation was found with the average daily maximum temperature at each site. The relative effectiveness of the organotin compounds and ultraviolet absorbers in preventing deterioration of the PVC was estimated by measuring the viscosity of the polymer after exposure. This method of assessment is compared with the results of mechanical tests on the specimens.

INTRODUCTION

In order to evaluate the weathering of plasticized PVC, flexible compositions containing a number of organotin compounds and ultraviolet absorbers have been exposed outdoors at Defence Standards Laboratories, Maribyrnong, Victoria (temperate climate) and at the Joint Tropical Research Unit (JTRU) sites at Cloncurry (hot-dry), and in the "open" and in the "jungle" at Innisfail, Queensland (hot-wet). Some details of the specimens together with the results of mechanical tests conducted on specimens exposed for 1.5 years have been reported before.[1]

Extraction of the plasticizers remaining in the specimens after exposure and comparison of the climatic conditions at the respective sites should indicate whether temperature is one of the most important factors in causing loss of plasticizer.

The viscosities of the residual polymer should show which compounds have been degraded most during exposure and enable an assessment to be made of the effectiveness of the additives in preventing deterioration of the polymer itself. Comparison with the conventional mechanical properties of the specimens should illustrate the practical application of this assessment.

EXPERIMENTAL

The formulation of the PVC basic composition (P15) was as follows:

Component	Parts by weight
PVC resin	100
Dioctyl phthalate	65
Octyl-9,10-epoxy stearate	10
Calcium carbonate	10
Tribasic lead sulfate	2.5
Dibasic lead phosphite	2.0
Calcium stearate	0.5
	190

The PVC resin used was Corvic P55/60, supplied by Imperial Chemical Industries of Australia and New Zealand.

The additives listed in Table II were added to the compound prior to extrusion. The bronze-green pigment had the following w/w composition: synthetic iron oxide AHK/F, 11.6%; synthetic iron oxide AK/F, 5.8%; carbon black (Acarb 300), 1.2%; chromium oxide green 5E, 81.4.

The ultraviolet absorbers (S_1, S_2, Table II) and the tri-*n*-butyltin fumarate half-ester, Advacide N628, were used in the forms supplied by the manufacturer. The organotin compounds were prepared by standard methods.[2]

The experimental compounds used for the weatherability trials were prepared as follows. The PVC resin and all the powders, with the exception of the organotin compound, were blended in a Winkworth "Z" type internal mixer. The organotin compound was dissolved in the mixed plasticizers by heating where necessary, cooled to 60°C, and added to the dry powder blend. After blending for $^1/_2$ hr, the viscous plastisol was poured from the blender into a shallow tray and gelled in an air oven for $^1/_2$ hr at 160°C. After cooling, the PVC compound was granulated and extruded through a slit die mounted on a $1^1/_8$ in. Telford-Smith screw extruder fitted with a general-purpose water-cooled screw. An air-cooled, variable-drive takeoff belt was used to produce a specimen strip 1.25 in. wide and 0.050 in. thick. The operating conditions of the extruder during the production of test strips were: screw speed, 44 rpm; filter gauze combination, 30–60–30 mesh; water outlet temperature from the screw, 25°C; power rating of the main drive, 1.9 amp; takeoff speed, 4 ft/min; rear-zone screw temperature, 155°C; front-zone screw temperature, 155°C; screw head temperature, 160°C; slit die temperature, 170°C.

Extruded samples, each 36 in. long, of each compound were exposed on racks at each site at an angle of 45°, facing north.

Standard test methods were used for the determination of tear strength,[3] tensile strength,[4] elongation at break,[4] and hardness,[5] both before and after exposure.

Standard methods were used to record the meteorologic data at the exposure sites during the period of the trial. Data are available from Defence Standards Laboratories for Maribyrnong (temperate), Innisfail (hot-

wet) in the "open" and in the "jungle," and for Cloncurry (hot-dry). Detailed long-term meteorologic data are also available.[6]

After exposure, specimens were returned to the laboratory for assessment. The plasticizers were removed by extraction using ether. A portion of the exposed strip (10 g) was cut into small pieces (0.5 × 0.5 cm) and extracted with ether (100 ml) in a Soxhlet apparatus for 8 hr. It was found that all the plasticizers in the specimen were removed in this time. The ether extract was then distilled on a steam bath, and the residue was weighed. The inherent viscosity, at 30°C, of the polymer was determined by dissolving a weighed sample of the extracted PVC compound in freshly distilled cyclohexanone (100 ml) and using the method described in ASTM D1243-66.[7] Thus, the sample (0.2 g) was transferred to a volumetric flask (100 ml), freshly distilled cyclohexanone (50 ml) was added, and the flask was heated to 85°C for $1^1/_2$ hr. The flask was then cooled to 20°C, and the solution volume was made up to the mark with cyclohexanone which had been heated exactly as the solution. An aliquot (10 ml) of the solution was decanted into a suspended-level viscometer incorporating a sintered glass filter disc,[8] the viscometer was placed in a water bath at 30°C, and after 10 min the flow time of the solution was measured. The flow time of the thermally aged cyclohexanone was measured in the same way. The inherent viscosity was then calculated as follows:

$$\text{relative viscosity} = \frac{t_1}{t_2}$$

$$\text{inherent viscosity} = \frac{\text{natural log relative viscosity}}{C}$$

where t_1 and t_2 are the measured flow times of the solution and solvent, respectively, and C is the concentration of PVC polymer in the extracted sample (g/100 ml) taken as calculated from the original formulation.

The IUPAC term for inherent viscosity is "logarithmic viscosity number."

RESULTS AND DISCUSSION

Loss of Plasticizers During Exposure

The loss of plasticizer for the control samples exposed at four different sites is given in Table I. Inasmuch as loss of plasticizer could be due primarily to evaporation, an attempt has been made to correlate this loss with typical climatic conditions at each site. Average daily maximum and average daily mean temperatures for the sites are given in Table I. A linear regression of percentage loss of plasticizer against these temperatures gave correlation coefficients of 0.994 for average daily maximum temperature and 0.987 for average daily mean temperature. The relation between loss of plasticizer and average daily maximum temperature is shown in Figure 1. This temperature would be expected to be related to the surface temperature of the PVC, and this should directly correlate with the rate of evaporation of the plasticizer.

TABLE I
Loss of Plasticizers During Exposure[a]

Site	Loss of plasticizer, %[b]	Temperature, °F: Average daily maximum	Temperature, °F: Average daily mean	Total rainfall[c]: in.	Total rainfall[c]: cm
Innisfail (hot-wet)					
"open"	23.0	82.5	73.8	566.3[d]	1438
"jungle"	20.5	79.0	73.0		
Cloncurry (hot-dry)	28.2	90.7	78.2	64.3	163.3
Maribyrnong (temperate)	9.7	67.6	58.8	115.5	293.4
Calculated values for another typical site, for example, Sydney, NSW	13.6	—	63.7		
	13.0	71.1	—		

[a] Determined on control PVC compound P15 after 4.5 years of exposure. The specimens at Maribyrnong (temperate) were exposed for 5 years and the results were adjusted for an exposure period of 4.5 years.

[b] Based on the total plasticizer in the original compound.

[c] Measured over the period of the exposure trial.

[d] Measured for the "open" site; some slight differences due to the jungle canopy might be expected at the "jungle" site.

Rainfall during the trial period, as listed in Table I, which could cause loss of water-resistant plasticizer by leaching from the surface, appears to have had little or no effect. Considered independently, the very low total rainfall at Cloncurry and the very high total rainfall at Innisfail do not appear to have had any influence on the correlation between loss of plasticizer and temperature.

In hot-wet tropical areas, loss of plasticizer can occur due to attack by fungi. Dioctyl phthalate is not very susceptible to fungal attack, and loss of this plasticizer for this reason at the "jungle" and "open" sites at Innisfail is, we believe, insignificant. Other climatic factors such as wind speed and duration, relative humidity, extent of cloud cover, and sunlight intensity could have some effect on the evaporation rate of plasticizers. However, the empirical correlation found between average daily maximum temperature and loss of plasticizer, combined with the other evidence, seems to exclude these other factors.

As the testing sites cover a wide range of Australian low-altitude climatic conditions, it should be possible by interpolation to predict the loss of plasticizer at a given site if the average daily maximum temperature is known. As shown in Table I, this has been undertaken for Sydney, New South Wales, and an estimate has also been made based on the average daily mean temperature.[7]

The results quoted apply to the control PVC formulation without special additives. Compounds with improved resistance to weathering show less surface damage, which is reflected in a reduced loss of plasticizer. The

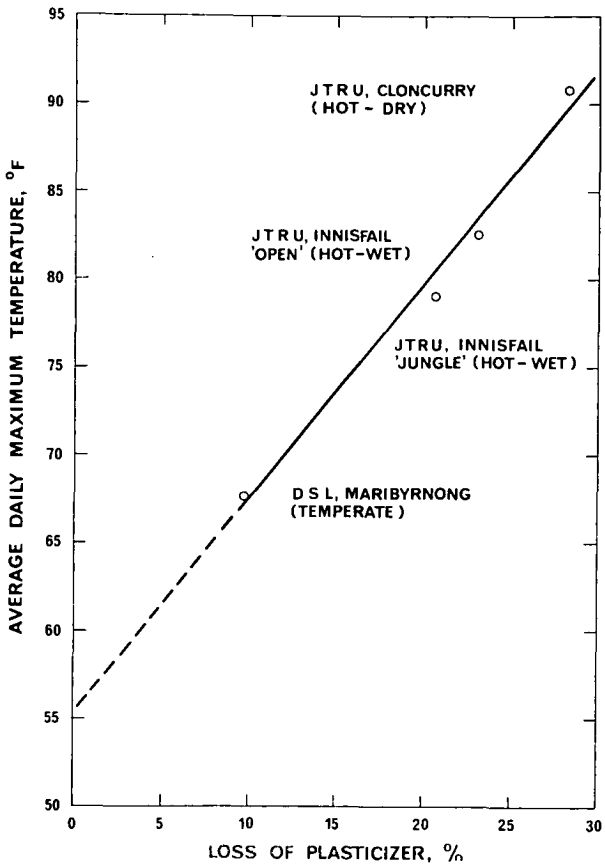

Fig. 1. Relation between average daily maximum temperature and loss of plasticizer for plasticized PVC compounds exposed for 4.5 years at four sites in Australia.

quality of the PVC compounds is thus of primary importance in the loss of plasticizer as a result of outdoor weathering.

From Figure 1, it would appear that PVC compositions containing dioctyl phthalate as the primary plasticizer, if stored below about 55°F, should show an insignificant rate of loss of plasticizer.

The results discussed apply to dioctyl phthalate which is one of the most commonly used plasticizers in Australia. By comparing the volatilities of other plasticizers with that of dioctyl phthalate, it should be possible to anticipate the long-term performance of these plasticizers over a wide range of climatic conditions.

Polymer Degradation During Exposure

Actinic degradation of PVC during exposure would be expected to cause changes in the molecular weight of the polymer. These changes should be able to be detected by viscosity measurements, and preliminary experi-

TABLE II
Plasticized PVC Exposed for 4.5 years[a]

Additive[b]	Inherent viscosity at each site × 100				Average viscosity	Overall rating
	Cloncurry (hot-dry)	Innisfail (hot-wet) "open"	Innisfail (hot-wet) "jungle"	Maribyrnong (temperate)		
S_1 + TBT fluoride	70.5	100.9	127.5	—	99.6	1
S_2 + TBT fluoride	68.9	97.1	116.0	—	94.0	2
S_1 + Ph_3SnF	70.7	105.4	98.0	89.2	90.8	3
S_1 + Poly(TBT methacrylate)	67.0	86.4	111.3	87.2	87.4	4
Bronze-green pigment	74.6	92.6	96.8	82.5	86.6	5
S_2 + Poly(TBT methacrylate)	75.7	78.7	97.4	94.3	86.5	6
S_2	68.9	97.1	91.0	—	85.6	7
Ph_3SnF	66.9	96.0	94.7	82.7	85.1	8
S_2 + Ph_3SnF	67.7	92.0	92.7	82.4	83.7	9
Poly(TBT acrylate)	65.9	92.1	95.3	80.5	83.4	10
TBT fumarate	63.2	88.4	96.3	79.9	81.9	11
Bis(TBT) terephthalate	46.1	90.9	102.8	80.1	79.9	12
TBT fluoride	61.5	92.4	80.7	—	78.1	13
Bis(TBT) oxide	62.9	77.9	94.6	74.5	77.5	14
Bis(TBT) maleate	58.2	87.0	86.3	75.8	76.8	15
Bis(TBT) sebacate	47.2	83.6	82.4	87.4	75.1	16
S_1	60.0	78.4	86.7	—	75.0	17
Poly(TBT methacrylate)	40.5	73.2	94.5	77.1	71.3	18
Control, no additive	57.8	67.3	71.7	—	65.6	19

[a] Control compound P15, containing 0.5% w/w of each additive as listed.

[b] S_1, 2-hydroxy-4-methoxybenzophenone: TBT, tri-*n*-butyltin; S_2, 2-(2′-hydroxy-5-methylphenyl)benzotriazole; Ph_3SnF, triphenyltin fluoride; bronze-green pigment was added at a concentration of 0.8% w/w (see experimental section for composition); TBT fumarate, tri-*n*-butyltin fumarate half ester, Advacide N628 (Advance Solvents and Chemical Company).

ments on unexposed PVC compounds showed that the inherent viscosity as determined was independent of the additive present. Viscosity data for specimens returned after long-term exposure at four separate sites are given in Table II.

Changes in the molecular weight of the polymer due to chain scission or to crosslinking as a result of actinic degradation are thus reflected in the inherent viscosity measurements. The specimens with the best resistance to weathering, as assessed by visual observation, had the highest viscosity. The viscosity values listed for each site are generally lowest at Cloncurry (hot-dry climate), and follow in increasing value at Maribyrnong (temperate), Innisfail (hot-wet) "open" and Innisfail "jungle." This general trend may reflect the climatic conditions at each site.

An average viscosity value for each compound over all the sites was then derived, and this was used to represent the overall performance of each additive. In Table II, the additives are arranged in descending order according to the average viscosity, and an overall rating is allocated to each. Although the lowest number in the overall rating scale indicates least degradation, care should be taken in interpreting results, as some variations in performance at different sites have been found.

Visual examination indicated that the surface color of the exposed specimens could vary from the original white to a dark brown, depending on the additive present. The surface discoloration of the compounds, particularly those exposed at Cloncurry, agreed well with the overall rating, as in all cases the lowest rating was associated with the least degree of surface discoloration. However, because of wide variations in surface texture and color at each site, inherent viscosity is seen as a more reliable parameter than surface color in assessing the relative efficiency of additives in reducing actinic degradation.

Of the best six compositions (Table II), five contained both an organotin compound and an ultraviolet absorber and performed better than compositions with one of these additives alone. This indicates that a powerful protective effect operates when these two classes of compound are present together. The use of the green pigment in the compound gave greater protection than either of the ultraviolet absorbers alone.

As shown in Table II, both tri-*n*-butyltin fluoride and poly(tri-*n*-butyltin methacrylate) in combination with either ultraviolet absorber were more effective in reducing actinic degradation than the ultraviolet absorbers alone. When used in combination with an organotin compound, the absorber S_1 (2-hydroxy-4-methoxybenzophenone) performed better than S_2 (2-(2′-hydroxy-5-methylphenyl)benzotriazole). However, when the ultraviolet absorbers were used alone with the standard PVC compound, the order of performance was reversed.

When the compositions containing only a single additive were considered, the order of rating of some of the additives was: green pigment (rating 5), ultraviolet absorber S_2 (rating 7), triphenyltin fluoride (rating 8), and ultraviolet absorber S_1 (rating 17). Thus, triphenyltin fluoride is exerting a

powerful protective effect and is only marginally worse than the better of the two ultraviolet absorbers. Triphenyltin fluoride also exhibits a protective effect with the ultraviolet absorbers.

Changes in Physical Properties During Exposure

With plasticized PVC, changes in the plasticizer content can have a marked effect on the mechanical properties. Because of the high loss of plasticizer caused by evaporation, the mechanical properties of the exposed compounds are affected by this loss as well as by degradation of the polymer. In order to investigate these effects, compounds were prepared having a reduced plasticizer content, as shown in Table III.

TABLE III
Modified Formulations with Lower Plasticizer Content

Component[a]	DSL compound no., parts by wt				
	P108	P109	P110	P111	P112
PVC	100	100	100	100	100
Dioctyl phthalate	53.6	54.1	55.8	58.0	57.4
Octyl-9,10-epoxy stearate	8	8	8	8	8
Calcium carbonate	10	10	10	10	10
Tribasic lead sulfate	2.5	2.5	2.5	2.5	2.5
Dibasic lead phosphite	2	2	2	2	2
Calcium stearate	0.5	0.5	0.5	0.5	0.5
Bis (TBT) oxide		0.95			
TBT fluoride			0.95	0.95	0.95
S_1				0.95	
S_2					0.95
Plasticizer content, % w/w	34.8	34.8	35.5	36.1	35.9

[a] TBT, tri-*n*-butyltin; S_1, 2-hydroxy-4-methoxybenzophenone; S_2, 2-(2′-hydroxy-5-methylphenyl)benzotriazole.

Table IV compares the results of mechanical tests on the original specimens, the exposed specimens from Cloncurry and modified nonexposed specimens containing a reduced amount of plasticizer.

As shown in Table IV, a reduction in the amount of plasticizer in the compound causes changes in physical properties of the unexposed compound. This indicates that mechanical measurements alone on exposed specimens should not be used as the sole evidence that the PVC itself has been degraded. In particular, the tensile and tear strengths of the specimens seem to be most affected by the reduction in plasticizer content.

The elongation at break, however, which might be expected to be reduced by crosslinking in the polymer, is greatly reduced in exposed specimens as compared to both the unexposed originals and the modified specimens. Compounds containing both organotin and ultraviolet absorber additives are less affected, suggesting that the protective effect as shown by viscosity rating is also being exhibited. This is apparent from the me-

TABLE IV
Mechanical Measurements

Additive[a]	Condition[b]	Plasticizer present, %	Tensile strength[3] psi	Tensile strength[3] kN/m²	Elongation at break,[4] %	Tear strength[4] lbf/in.	Tear strength[4] kN/m	Hardness[5] IRHD
Control	original	39.5	2120	14 600	348	276	48.3	79
Control	exposed	28.2	—	—	—	430	75.3	90
Control	modified	34.8	2260	15 600	304	289	50.6	82
Bis(TBT) oxide	original	39.3	2040	14 050	331	269	47.1	77
Bis(TBT) oxide	exposed	28.3	2000	13 800	60	430	75.3	96
Bis(TBT) oxide	modified	34.8	1980	13 650	326	330	57.7	79
TBT fluoride	original	39.3	2180	15 000	367	278	48.6	77
TBT fluoride	exposed	29.2	1950	13 450	80	300	52.5	95
TBT fluoride	modified	35.5	2150	14 800	318	306	53.5	77
S_1 + TBT fluoride	original	39.1	2250	15 500	336	287	50.2	76
S_1 + TBT fluoride	exposed	30.2	1970	13 600	90	390	68.2	85
S_1 + TBT fluoride	modified	36.1	1920	13 250	292	256	44.8	73
S_2 + TBT fluoride	original	39.1	2210	15 250	350	293	51.3	76
S_2 + TBT fluoride	exposed	29.9	1870	12 900	120	360	63.1	86
S_2 + TBT fluoride	modified	35.9	1910	13 150	296	250	43.7	72

[a] Control compound P15 containing 0.5% w/w of each additive as listed.

[b] Original, measured before exposure; exposed, measured after 4.5 years of exposure at Cloncurry; modified, measured without exposure on compounds containing reduced amount of plasticizer as listed in Table III.

chanical measurements. The elongation at break can thus be recommended as a meaningful mechanical test for evaluating the resistance of plasticized PVC to weathering.

The assistance of the staff at JTRU at Innisfail in arranging the exposures is acknowledged.

References

1. P. Dunn and E. J. Hill, *Fungicides for Use with Poly(vinyl Chloride)*, Report No. 298, Defence Standards Laboratories, Department of Supply, Melbourne, Australia, 1967.

2. P. Dunn and T. Norris, *The Preparation of Organotin Compounds*, Report No 269, Defence Standards Laboratories, Department of Supply, Melbourne, Australia, 1964.

3. British Standards Institution, British Standard 2782, *Methods of Testing Plastics*, Part 3, Mechanical Properties, Method 301 D, London, 1957.

4. *Ibid.*, Method 308A.

5. British Standards Institution, British Standard 903, *Methods of Testing Vulcanised Rubber*, Part A20, London, 1959.

6. Bureau of Meteorology, *Climatic Averages Australia*, Melbourne, Australia, 1969.

7. ASTM Standards on Plastics, Part 27, Method D1243-66, *Dilute Solution Viscosity of Vinyl Chloride Polymers*, American Society for Testing Materials, Philadelphia, 1969.

8. G. W. Harding, *J. Polym. Sci.*, **55**, S27 (1961).

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APPENDIX 14d

(14 pages)

PRI

International symposium

The weathering of plastics and rubbers

8 and 9 June 1976

Institution of Electrical Engineers

London WC2R OBL

The Plastics and Rubber Institute
11 Hobart Place, London SWIWOHL

Papers for the symposium issued as a bound set of preprints to participants.

Paper D5 retyped from a grid sheet copy,
February, 1978.

THE WEATHERING OF PLASTICS AND RUBBERS

SESSION D (B)

EFFECTS OF WEATHERING AND THEIR PREDICTION - POLYVINYLCHLORIDE

D5 Weathering of improved plasticised poly(vinyl chloride)
P DUNN, DR D OLDFIELD & G F SANSOM
Department of Defence, Materials Research Laboratories, Australia

D6 Techniques for predicting the weathering performance of rigid PVC
G BUTTERS & GC MARKS
BP Chemicals International Ltd

D7 The prediction of PVC weathering
DR JC MARECHAL & DR Ph EURIN
Centre Scientifique et Technique du Batiment, France

D8 Paper withdrawn

THE WEATHERING OF PLASTICS AND RUBBERS

WEATHERING OF IMPROVED PLASTICISED POLY(VINYL CHLORIDE)

P. Dunn,* D. Oldfield* and G.F. Sansom*

Thirty-two plasticised poly(vinyl chloride) compounds have been exposed for 5 yr to a variety of Australian climates ranging from hot-dry and hot-wet to temperate. The visual appearance, mechanical properties and microbiological deterioration of the specimens are reported, together with an assessment of the relative performance of the specimens to weathering. Many of the PVC compounds showed excellent resistance to weathering. The five best formulations all contained, as a secondary plasticiser, an organoarsenic epoxidised soya bean oil derivative with barium metaborate as a filler and compounds such as the fungicide copper-8-hydroxyquinolinate, with or without an ultraviolet absorber.

INTRODUCTION

Plasticised poly(vinyl chloride) (PVC) finds many uses in military, industrial and commercial equipment where it is required to withstand adverse conditions of weathering and microbiological attack. Trials conducted previously by these laboratories (1,2,3) have investigated the weathering of plasticised PVC under different environmental conditions in Australia. Following these trials some new PVC formulations were prepared which were expected to show improved resistance to environmental degradation. This report describes the preparation, exposure and properties of these PVC compounds in trials conducted for 5 yr under a variety of Australian climatic conditions.

EXPERIMENTAL

All the plasticised PVC compounds were formulated and processed at MRL; the formulations are given in Appendix 1. Compounding ingredients (Appendix 2) were used in the form supplied by the manufacturer.

The basic formulation consisted of PVC resin, a plasticiser (dinonyl phthalate) and a stabilizer system (tribasic lead sulphate and dibasic lead phosphite) shown previously (1,2,3) to be very suitable for use under Australian conditions. Selected secondary plasticisers, fillers, pigments, ultraviolet absorbers and other stabilizing additives were then used to produce the thirty-two compounds used for the trial. Four compounds, namely *[27]*, *[28]*, *[29]* and *[30]*** were produced in an olive-green colour by the use of a selected pigment known to be satisfactory (1).

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** For convenience, formulation numbers (Appendix 1) are indicated thus *[ ]*

The colour of the remaining compounds was generally white except where the additives imparted a slight tint.

The compounds were prepared as follows. The PVC resin and all the powders were blended in a Winkworth "Z"-type internal mixer, and the mixed plasticisers were then added. After blending for 0.5h, the viscous plastisol was poured into a shallow tray and gelled in an air oven for 0.5h at 160°C. After cooling, the PVC compound was granulated and extruded through a slit die mounted on a 28 mm Telford-Smith screw extruder, fitted with a general purpose water-cooled screw. An air-cooled, variable-drive, take-off belt was used to produce a specimen strip 32 mm wide and 1.3 mm thick. The operating conditions of the extruder during the production of test strips were : screw speed, 44 rpm; filter gauze combination, 30-60-30 mesh; water outlet temperature from the screw, 25°C; power rating of the main drive 1.9 amps; take-off speed, 1.2 m/min; rear zone screw temperature, 155°C; screw head temperature, 160°C; slit die temperature, 170°C.

Extruded samples, 0.9 m long, of each compound were attached by their ends to racks in such a way that the main part of the specimen was free from obstruction. Specimens were exposed at an angle of 45°, facing north at MRL, Maribyrnong, Victoria (temperate) in the open (hot-wet, open) at the Joint Tropical Research Unit (JTRU), Innisfail, North Queensland and at JTRU, Cloncurry, Queensland (hot-dry). Specimens mounted vertically were exposed at a site in the jungle (hot-wet, jungle) at JTRU, Innisfail and were also buried horizontally in the soil in the jungle at a depth of 0.1 m. A complete set of specimens was stored indoors at MRL, Maribyrnong, as controls.

Standard meteorological data at each exposure site were recorded and detailed information is available from MRL. Typical data for the five year period 1970-74 are given in Table 1.

TABLE 1 - Meteorological Data, 1970-74, Exposure Sites - Australia.

Location	Latitude, S	Average Daily Maximum Temperature	Average Index of Relative Humidity	Total Rainfall	Total Sun
		°C	%	mm	h
Maribyrnong, Victoria (near Melbourne)	37°49'	20	55	3600	11400
Innisfail, Queensland ('open' site)	17°31'	28	82	18150	11720
Cloncurry, Queensland	20°41'	33	37	2940	17360

To determine the plasticiser content of the specimens, a strip (10 mm x 50 mm) cut into small pieces (5 mm x 10 mm was extracted with diethyl ether (150 ml in a hot soxhlet apparatus for 16 h. The extract was then evaporated to dryness in a rotary evaporator, dried in an air circulating oven at 70°C for 2 h, and weighed.

Standard test methods were used for the determination of tear strength (4), tensile strength (5), elongation at break (5) and hardness (6) of the specimens before and after exposure.

RESULTS AND DISCUSSION

Visual assessment

All the specimens were examined after exposure for 5 yr and selected properties assessed using a rating scale 0-4, where 0 represented no change and 4 represented severe change. For specimens exposed above ground, assessments were made for degree of crazing, change in stiffness and change in colour. Specimens buried in the soil were assessed for change in stiffness, staining and resistance to attack by termites. A combined rating for each compound exposed at each site was thus obtained, together with the total rating for the compound for all sites. The compounds with the lowest total ratings would be regarded as being apparently least affected by the conditions of exposure. Details of ratings appear in Table 2.

The results obtained from specimens buried in the soil suggested that those compounds containing the organoarsenic soya bean derivative and barium metaborate were more susceptible to termite attack than those containing octyl-9,10-epoxy stearate and calcium carbonate.

Microbiological assessment

Assessments of amount of debris, fungal growth and algal growth on the specimens exposed at the hot-wet cleared, hot-wet jungle and soil burial sites were made, recorded and used as part of the overall assessment of performance of each compound.

With specimens exposed at the jungle site, *Rhinocladiella* and *Cladosporium* were the main genera present, although others were isolated which were most likely derived from incidental spores, including *Epicoccum, Alternaria, Phialophora, Myrothecium, Fusarium* and *Streptomyces*.

With specimens exposed at the cleared site, several genera were isolated but none was predominant. For specimens buried in the soil, *Scopulariopsis* was the main genus isolated but *Aspergillus, Paecilomyces, Penicillium* and *Cladosporium* were also frequently recovered.

Microscopic examination

Photomicrographs of sections, 10μm thick, cut from specimens, were taken and examined to study the extent of surface degradation and its depth of penetration. In many cases the surface exposed to the sun was found to be extensively eroded whilst the shaded surface still appeared smooth. A band of material either lighter or darker than the body of the specimen was usually found below the eroded surface. This effect in the sub-surface was most pronounced in specimens returned from the hot-dry site and least in those from the soil burial and jungle sites, suggesting that actinic degradation was the main factor responsible for the severe erosion. A representative selection of photomicrographs is shown in Figures 1 and 2.

Tear strength

Values of the tear strengths of all the specimens as originally prepared and the changes during storage at MRL and exposure were determined. There was

little change after storage for 1 yr but a mean fall of 18% after storage for 5 yr. Almost all of the exposed specimens showed an increase in tear strength which was greatest for those from the soil burial site (mean 61%), followed by those from the hot-wet, open (56%), hot-dry (40%), hot-wet, jungle (29%) and temperate (17%) sites.

Tensile strength

Values of the original tensile strengths and the changes resulting from storage or exposure were determined. The tensile strength of the specimens generally increased on storage or exposure, with the mean increases on storage for 1 and 5 yr being 9% and 8% respectively. Specimens from the soil burial site showed the largest increase in tensile strength (mean 40%), with those from the hot-wet, jungle (27%), hot-wet, open (19%), hot-dry (14%) and temperate (11%) sites following in decreasing order.

Hardness

The hardness of the specimens stored for 1 and 5 yr decreased by mean values of 8% and 4% respectively. The surface of the specimens exposed to the sun at the hot-dry, hot-wet, open and temperate sites generally increased in hardness more than the shaded surface but the mean increases for the sites were similar. For soil burial specimens the hardness was similar on both surfaces. They showed a slightly greater increase (mean 22%) than those from the other sites, namely hot-dry (exposed, 19%; shaded, 15%), hot-wet, open (21%; 20%), hot-wet, jungle (17%; 15%) and temperate (12%; 10%).

Elongation at break

Elongation at break tended to be reduced after storage for 1 yr (mean decrease 11%) but there was no clear trend in the specimens stored for 5 yr (mean increase 3%). Almost all of the exposed specimens showed a decrease in the elongation at break with the largest decreases being shown by those from the hot-dry site (56%) followed by the hot-wet, open (40%), temperate (28%), hot-wet, jungle (8%) and soil burial (8%) sites. These results show the order expected if actinic degradation is a major factor responsible for the changes in elongation at break in the specimens.

Relative energy to break

The stress-strain curve for each specimen was plotted from measurements taken during the determination of tensile strength and the area under each curve was measured with a planimeter. Representative sets of stress-strain curves are shown in Figures 3 and 4. The area is related to the energy required to break the specimen. The areas under the curves for the stored and exposed specimens of each compound were compared to the area from the original specimen in each case and the changes in area and hence in the energy to break were calculated. The largest changes were found for the soil burial specimens where a mean increase of 58% was recorded. The changes from the other sites, arranged in decreasing order of change, were hot-wet, jungle (+ 35%), temperate (- 20%), hot-wet, open (- 26%) and hot-dry (- 40%). The high value for specimens buried in the soil suggests that loss of plasticiser produces an increase in the energy to break whereas solar degradation produces a decrease. The energy to break is related both to the tensile strength and the elongation at break of the specimen and it may prove to be a useful indicator for assessing the relative performance of PVC compounds.

Tabulated data on the mechanical properties described above, are available

Residual plasticiser

The plasticiser contents of all the stored and exposed specimens determined by extraction indicated that the greatest losses were recorded for the soil burial specimens (mean 21%) followed by the hot-wet, open (18%), hot-dry (14%), temperate (10%) and hot-wet, jungle (10%).

Performance rating

Several different schemes were used to assess the relative performances of the compounds so that the one most resistant to exposure at all sites could be identified. In Table 2 the first column lists the formulation code numbers and subsequent columns contain the performance ratings of the PVC compounds. The lowest numbers in each column indicate the greatest weathering resistance.

In the second column the ratings were determined from the visual assessment carried out on the specimens after exposure for 5 yr. From this assessment formulations *[4]* and *[22]* performed best at all sites followed by *[16]*, *[19]* and *[20]*, and *[18]*. The third column contains the ratings derived from the changes in elongation at break for the specimens after exposure for 5 yr. In a previous trial (2) this type of rating was found to correlate well with both the visual assessment and the changes in the molecular weight of the PVC as measured by solution viscosity. The performance in decreasing order was *[22]*, *[16]*, *[23]*, *[28]* and *[30]*.

The fourth column lists the ratings derived from the changes in energy to break. The best formulations by this assessment were *[26]*, *[20]*, *[15]*, *[18]* and *[16]*.

These three ratings were then combined to produce a new final rating which appears in column five with the best formulation again being rated 1. The two formulations which had the highest rating were *[16]* and *[22]*, followed by *[26]*, *[18]*, *[15]* and *[20]*.

The original values of the mechanical properties together with the percentage changes after exposure for 5 yr at the various sites for six of the formulations are shown in Table 3. Formulations *[16]* and *[22]* showed the best performance to weathering, *[4]* and *[23]* were about average and *[7]* and *[9]* were among the poorest performers.

From the overall assessment of the thirty-two compounds used in the trial, the five which were most resistant to weathering all contained the organo-arsenic soya bean derivative as a secondary plasticiser and barium metaborate filler. The additives which gave the improved resistance to weathering were copper-8-hydroxyquinolinate in *[16]*, 2,4-thiazolyl benzimidazole and 2-hydroxy-4-methoxybenzophenone in *[22]*, copper-8-hydroxyquinolinate and 2-hydroxy-4-methoxybenzophenone in *[26]*, 2-hydroxy-4-methoxybenzophenone alone in *[18]* and nickel dibutyldithiocarbamate and 2-hydroxy-4-methoxybenzophenone in *[20]*. The next best formulation was *[15]* containing octyl-9,10-epoxy-stearate as the secondary plasticiser and calcium carbonate filler with copper-8-hydroxyquinolinate. Thus copper-8-hydroxyquinolinate in combination with each secondary plasticiser gave PVC compounds with excellent resistance to weathering. Providing the colour usually imparted by copper-8-hydroxyquinolinate to a plasticised PVC is not a disadvantage, the use of this additive to extend the outdoor life of PVC compounds should be considered.

It has been claimed (7) that plasticised PVC can be protected against

TABLE 2 - Relative performance* of PVC compounds exposed at all sites

Formulation Code	Visual Assessment Rating	Elongation at break Rating	Energy to break Rating	Final Rating
[1]	14	22	22	20
[2]	11	19	21	17
[3]	12	11	20	12
[4]	1	23	8	9
[5]	11	21	32	22
[6]	6	23	12	10
[7]	13	27	29	24
[8]	8	18	16	11
[9]	14	26	26	23
[10]	18	20	11	16
[11]	16	10	17	12
[12]	5	11	13	7
[13]	11	21	23	18
[14]	6	24	25	18
[15]	5	12	3	4
[16]	2	2	5	1
[17]	9	6	30	13
[18]	4	9	4	3
[19]	3	13	31	15
[20]	3	15	2	4
[21]	11	22	28	21
[22]	1	1	7	1
[23]	5	3	24	9
[24]	17	14	27	20
[25]	5	17	9	8
[26]	7	7	1	2
[27]**	15	16	15	14
[28]**	10	4	18	9
[29]**	9	8	6	5
[30]**	8	5	14	6
[31]	12	25	19	19
[32]	9	10	10	7

* In any column, rating 1 signifies the best performance.
** Olive-green compounds.

TABLE 3 - Selected values of mechanical properties

Formulation Code	Original Value	Change after 5 yr exposure				
		Temperate[a]	HWJ[b]	HWC[c]	SB[d]	HD[e]
Tear strength	kN/m	%	%	%	%	%
[16]	43.7	+ 4.1	+12.8	+46.5	+38.6	+21.3
[22]	44.7	+ 5.1	+ 9.6	+27.5	+44.4	+34.2
[4]	40.4	+ 2.7	+23.0	+43.6	+52.5	+23.8
[23]	37.9	+18.7	+21.1	+66.2	+55.8	+31.9
[7]	40.9	+32.0	+13.4	+63.8	+70.7	+76.0
[9]	45.9	+25.3	+38.3	+74.3	+84.8	+54.7
Tensile strength	MPa					
[16]	11.6	+ 4.3	+19.8	+19.8	+31.0	+11.2
[22]	11.7	+12.8	+22.2	+17.9	+35.0	+13.7
[4]	10.7	+ 0.9	+21.5	+18.7	+31.8	+ 5.6
[23]	10.3	+35.9	+37.9	+48.5	+55.3	+27.2
[7]	11.3	+ 5.3	+30.1	+11.5	+47.8	+22.1
[9]	11.6	+ 2.6	+32.8	+19.0	+44.0	+19.0
Elongation at break	%					
[16]	305	-21.3	- 1.6	-27.9	- 1.6	-37.7
[22]	317	-14.8	- 2.2	-24.3	+ 0.9	-46.4
[4]	300	-36.7	-20.0	-43.3	-13.3	-56.5
[23]	300	-10.0	- 6.6	-20.0	- 6.7	-23.3
[7]	330	-45.5	- 9.1	-60.6	-12.1	-87.9
[9]	353	-43.3	- 9.3	-54.7	-12.2	-80.2
Relative energy to break						
[16]	-	- 6.4	+34.6	+ 6.7	+51.0	-16.4
[22]	-	+ 4.9	+30.3	+ 8.6	+54.2	-32.1
[4]	-	-23.8	+12.9	-13.3	+38.0	-44.1
[23]	-	+36.7	+45.5	+49.7	+72.9	+11.6
[7]	-	-26.6	+34.9	-39.1	+64.6	-76.8
[9]	-	-26.6	+45.9	-23.8	+66.3	-66.1

a) Temperate, MRL, Maribyrnong, Victoria.
b) Hot-wet, jungle, JTRU, Innisfail, Queensland.
c) Hot-wet, open, JTRU, Innisfail.
d) Soil burial, JTRU, Innisfail.
e) Hot-dry, JTRU, Cloncurry, Queensland.

microbial attack by incorporation of an organoarsenic soya bean oil derivative such as that used in the present trial. A very recent article (8) also describes the mould resistance of PVC films containing either an epoxidised soya bean oil dispersion of 10,10'-oxybisphenoxyarsine or the grade of barium metaborate used in our trial. The latter authors conclude that the good light stability of barium metaborate prolongs the inhibition of microbial growth on compounds containing this chemical.

These trials have indicated that certain combinations of plasticisers and fillers (for example, an organoarsenic soya bean derivative and barium metaborate) impart excellent resistance to weathering in flexible PVC compounds. The mode of action of these chemicals in stabilizing PVC, needs further detailed investigation.

In addition, the stabilizing action of copper-8-hydroxyquinolinate, which is normally considered to be a fungicide, has also been identified. Detailed investigation of this aspect should result in the development of PVC compounds with even further resistance to weathering.

ACKNOWLEDGEMENTS

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REFERENCES

1. Dunn, P and Hill, E.J., 1967. "Fungicides for use with Poly(vinyl chloride)", Defence Standards Laboratories, Department of Supply, Maribyrnong, Victoria, Report 298.

2. Dunn, P., Oldfield, D. and Stacewicz, R.H., *J. Appl. Polym. Sci.*, 14, (1970) 2107.

3. Dunn, P. and Hill, E.J. 1970. "Properties of Weathered Poly(vinyl chloride)", Defence Standards Laboratories, Report 410.

4. "Methods of Testing Plastics, Part 3, Mechanical Properties". British Standards Institution, London, BS2782, method 308A.

5. Ibid., method 301D.

6. "International Hardness of Vulcanized Rubber". American Society of Testing and Materials, Philadelphia, ASTM D 1415-68.

7. Sweitser, D., *Rubb. Plast. Age*, 49, (1968) 426.

8. Wienert, L.A. and Hillard, M.W., *Aust. Plast. Rubb.*, 26 (10), (1975) 15.

9. Dunn, P. and Norris, T., 1964. "The Preparation of Organotin Compounds". Defence Standards Laboratories, Report 269.

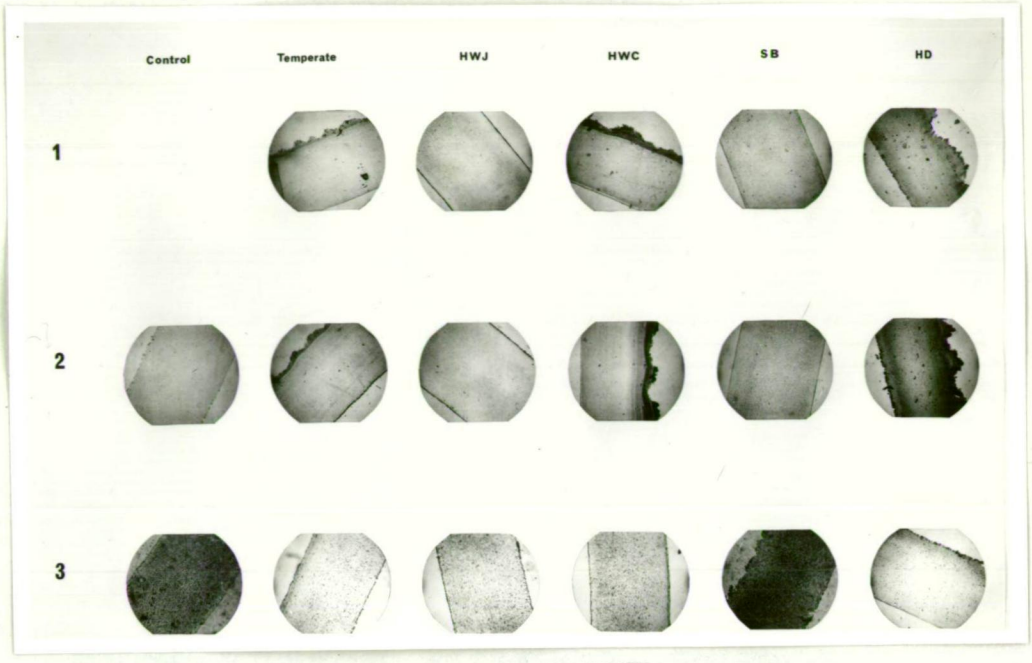


Figure 1. Photomicrographs of cross sections of PVC specimens (originally 1.3 mm thick) exposed for 5 yr at the sites as shown, HWJ (hot-wet, jungle), HWC(hot-wet, open), SB (soil burial), HD (hot-dry), for formulations *[1]*, *[2]* and *[3]*.

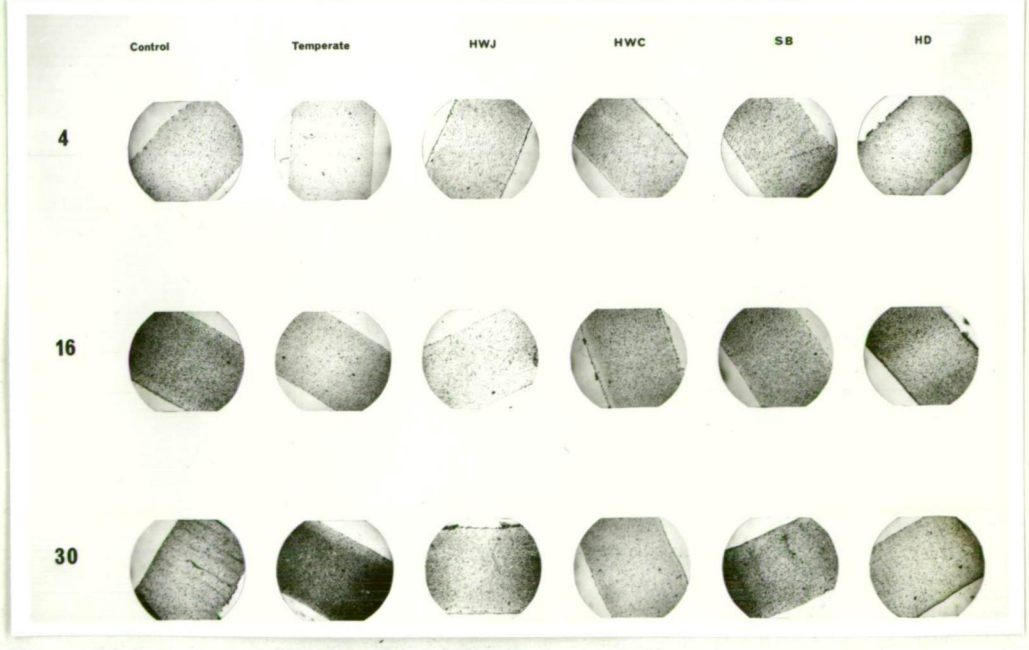


Figure 2. Photomicrographs of cross-sections of PVC specimens (originally 1.3 mm thick) exposed for 5 yr at the sites as shown, HWJ (hot-wet, jungle) HWC (hot-wet, open), SB (soil burial), HD (hot-dry), for formulations *[4]*, *[16]* and *[30]*.

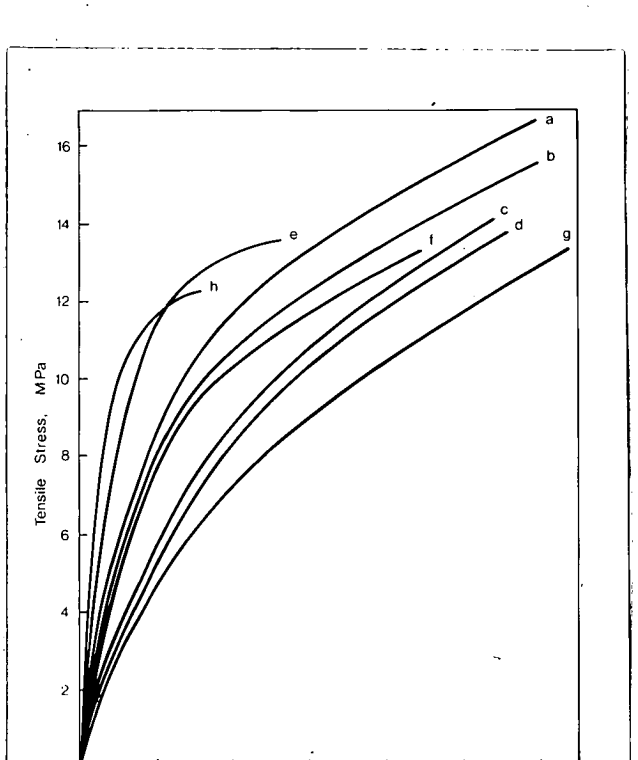


Figure 3. Stress-strain curves for formulation *[2]* specimens:

(a) soil burial, Innisfail; 5 yr
(b) hot-wet, jungle, Innisfail; 5 yr
(c) control; 1 yr
(d) control; as originally extruded
(e) hot-wet, open, Innisfail; 5 yr
(f) temperate, Maribyrnong; 5 yr
(g) control; 5 yr
(h) hot-dry, Cloncurry; 5 yr

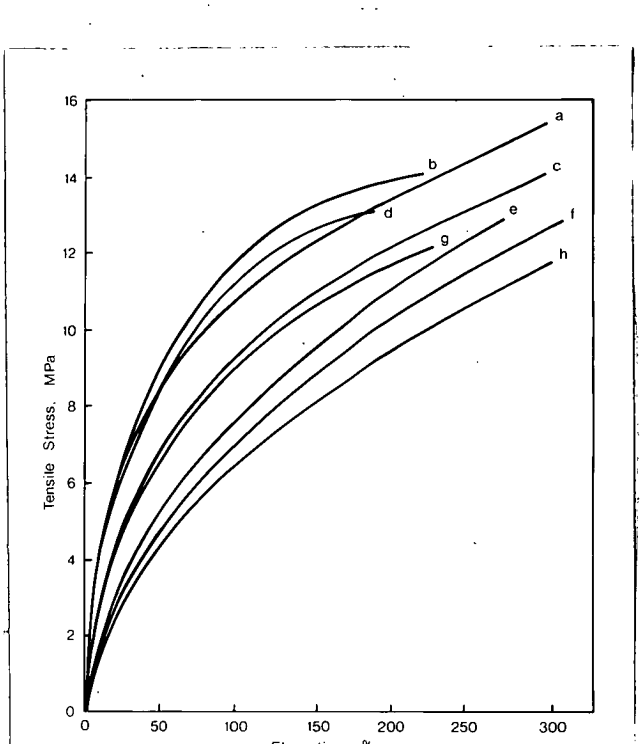


Figure 4. Stress-strain curves for formulation *[16]* specimens:

(a) soil burial, Innisfail; 5 yr
(b) hot-wet, open, Innisfail; 5 yr
(c) hot-wet, jungle, Innisfail; 5 yr
(d) hot-dry, Cloncurry; 5 yr
(e) control; 1 yr
(f) control; 5 yr
(g) temperate, Maribyrnong; 5 yr
(h) control; as extruded.

APPENDIX 1 - Formulations

Each compound contained the following ingredients:-

	Parts by weight
Poly(vinyl chloride) resin	100
Dinonyl phthalate plasticiser	65
Tribasic lead sulphate	2.5
Dibasic lead phosphite	2.0
Calcium stearate	0.5

The additional ingredients, expressed as parts per hundred parts of resin, in each formulation were :-

Formulation Code	a	b	c	d	e	f	g	h	i	j	k	l	m
[1]	10		10										
[2]		10	10										
[3]	10			10									
[4]		10		10									
[5]	10		10		0.95								
[6]		10		10	0.95								
[7]	10		10			0.95							
[8]		10		10		0.95							
[9]	10		10	10									
[10]		10	10	10									
[11]	10		10				0.95						
[12]		10		10			0.95						
[13]	10		10					0.95					
[14]		10		10				0.95					
[15]	10		10						0.95				
[16]		10		10					0.95				
[17]	10		10							0.95			
[18]		10		10						0.95			
[19]	10		10				0.95			0.95			
[20]		10		10			0.95			0.95			
[21]	10		10					0.95		0.95			
[22]		10		10				0.95		0.95			
[23]	10		10						0.95	0.95			
[24]	10		10								0.95		
[25]		10		10							0.95		
[26]		10		10					0.95	0.95			
[27]*	10		10									1.5	
[28]*	10		10							0.95		1.5	
[29]*		10		10								1.5	
[30]*		10		10						0.95		1.5	
[31]	10		10										0.95
[32]		10		10									0.95

(a) Octyl-9,10-epoxy stearate
(b) Organoarsenic epoxidised soya bean oil derivative
(c) Calcium carbonate
(d) Barium metaborate
(e) Tributyltin fluoride
(f) N-(trichloromethylthio) phthalimide
(g) Nickel dibutyldithiocarbamate
(h) 2,4'-Thiazolyl benzimidazole
(i) Copper-8-hydroxyquinolinate
(j) 2-Hydroxy-4-methoxy benzophenone
(k) 2,2'-Thiobis(4-t-octylphenolato)-*n*-butylamine nickel (II)
(l) Olive-green pigment: % by weight
Synthetic iron oxide, AHK/F 11.6
Synthetic iron oxide, AK/F 5.8
Carbon black 1.2
Chromium oxide 81.4
(m) Nickel bisoctyl phenyl sulphide
* Olive-green compounds

APPENDIX 2 - Compounding Ingredients

Material	Trade Name	Local Supplier
oly(vinyl chloride) resin	Corvic P65/50	ICI Australia Ltd
inonyl phthalate	Corflex 910	CSR Chemicals Ltd
ribasic lead sulphate	Mollistab X	Fletcher Chemical Co Ltd
ibasic lead phosphite	Molliphos	Fletcher Chemical Co Ltd
ctyl-9,10-epoxy stearate	Lankroflex ED3	Beith Chemical Materials Ltd
rganoarsenic epoxidised soya ean oil derivative	Estabex ABF	Brown and Dureau Ltd
alcium carbonate	Winnofil S	ICI Australia Ltd
arium metaborate - modified	Busan 11-M1	Hardie Trading Company
ributyltin fluoride	-	Synthesized at MRL (9)
-(trichloromethylthio) hthalimide	Fungitrol 11	Hatrick A.C. Chemicals Pty Ltd
ickel dibutyldithiocarbamate	NBC	Du Pont (Aust) Ltd
,4'-Thiazolyl benzimidazole	Thiabendazole	Ciba-Geigy Australia Ltd
ɔpper-8-hydroxyquinolinate	Cu-8	Watts Winter and Company
-Hydroxy-4-methoxy benzophenone	Cyasorb UV9	Cyanamid Aust Pty Ltd
,2'-Thiobis(4-t-octyl-phenolato)- -butylamine nickel (II)	Cyasorb UV1084	Cyanamid Aust Pty Ltd
ynthetic iron oxide	AHK/F, AK/F	Hodgsons Dye Agencies Pty Ltd
ırbon black	Acarb 300	Australian Carbon Black Pty Ltd
romium oxide	Green 5E	Hodgsons Dye Agencies Pty Ltd
ckel bis octyl phenyl sulphide	Ferro AM101	Ferro Corporation (Aust) Pty Ltd

APPENDIX 15 STRESS CRACKING OF POLYAMIDES - FAILURES OF COMPONENTS

15a	Components of Telephone Set K.	15.2
15b	Failures in Stressed Nylons. P. DUNN, A.J.C. HALL and T. NORRIS *Nature*. 195, No. 4846, 1092-1093 (1962)	15.3
15c	Stress Cracking of Nylon Components	15.4
15d	Case and Seal Materials for Telephone Set K. Part I. Case Materials. P. DUNN, T. LIGGINS and T. NORRIS Report 300. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.	15.5 - 15.7
15e	Rupture of Moulded Nylon Safety Glass Frames.	15.8

15.2

Appendix 15a - Telephone Set K used by the Australian Army. Components are: main case, handset and main case seals (4 off) (mag., x 0.65).

APPENDIX 15b

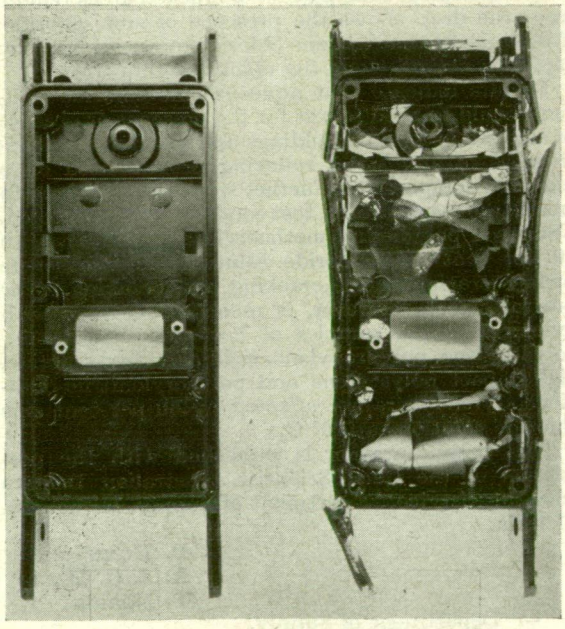
(*Reprinted from Nature, Vol.* 195, *No.* 4846, *pp.* 1092–1093, *September* 15, 1962)

Failures in Stressed Nylons

ENSANIAN[1] has observed that concentrated hydrochloric acid alone, or a mixture of hydrochloric acid, alcohol and zinc dust, caused rapid failure of a stressed nylon strip. In this connexion the results of some work we have been doing independently should be of interest.

Several nylon mouldings had been observed to crack and delaminate when in contact with electrolyte from discharged dry cells. Investigation of a number of possible causes of this cracking has shown that aqueous zinc chloride solutions, varying in concentration from 20 to 80 per cent, are effective in producing the failures observed (Fig. 1).

Mouldings that have been suitably stress-relieved are not affected by 80 per cent zinc chloride solution. The types of failure shown in Fig. 1 *B* occur with nylon 6, nylon 66, and nylon 11 under stress, and



A *B*

Fig. 1. Nylon 6 mouldings (length, 23 cm.). *A*, Untreated; *B*, treated with 80 per cent zinc chloride solution (one drop of solution at each of eight points for 24 hr. at room temperature). After cracking the moulding in Fig. 1 *B* had increased in length by 2 per cent

APPENDIX 15b

nylon components made by different techniques such as plunger and screw pre-plasticized injection moulding or by extrusion moulding can exhibit this stress cracking.

Saturated aqueous solutions of other chlorides and zinc salts have been examined and shown to be ineffective on stressed nylon mouldings. These include: ammonium chloride, aluminium chloride, cupric chloride, barium chloride, calcium chloride, magnesium chloride, manganese chloride, nickel chloride, ferric chloride, zinc nitrate, zinc acetate, zinc permanganate, and zinc sulphate.

Zinc chloride solutions are acidic, but they are much more effective than hydrochloric acid alone or the mixture used by Ensanian[1] in causing failure. The effect of single drops of 80 per cent zinc chloride solution when placed on a stressed nylon moulding is dramatic. This effect is very sensitive to temperature; mouldings that crack in 3–4 hr. at room temperature (20° C), crack in 30 min. at 35° C. and in 5 min. at 50° C.

When a single drop of 80 per cent zinc chloride solution is applied to a stressed nylon moulding, cracking can occur at points up to 15 cm. from the drop. Chemical examination of cracked areas remote from the drop shows the presence of zinc chloride. This suggests that the zinc chloride moves rapidly, by capillary action, along the cracks as they grow.

Results indicate that aqueous zinc chloride solutions could be used to test for the presence or absence of stresses in nylon mouldings and also for the effectiveness of any stress relieving process used on a moulded component. Further work is being done to enable the most suitable test conditions to be selected.

Stressed polymethyl methacrylate in contact with 80 per cent zinc chloride solution exhibits severe surface crazing before cracking and breaking. The rate of attack, however, is much slower than with nylon. Stressed samples of low- and high-density polyethylene, polypropylene, rigid polyvinyl chloride, high-impact polystyrene and polyacrylonitrile-butadiene-styrene were not affected by 80 per cent zinc chloride solutions at 20° C.

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Australia.

[1] Ensanian, M., *Nature*, **193**, 161 (1962).

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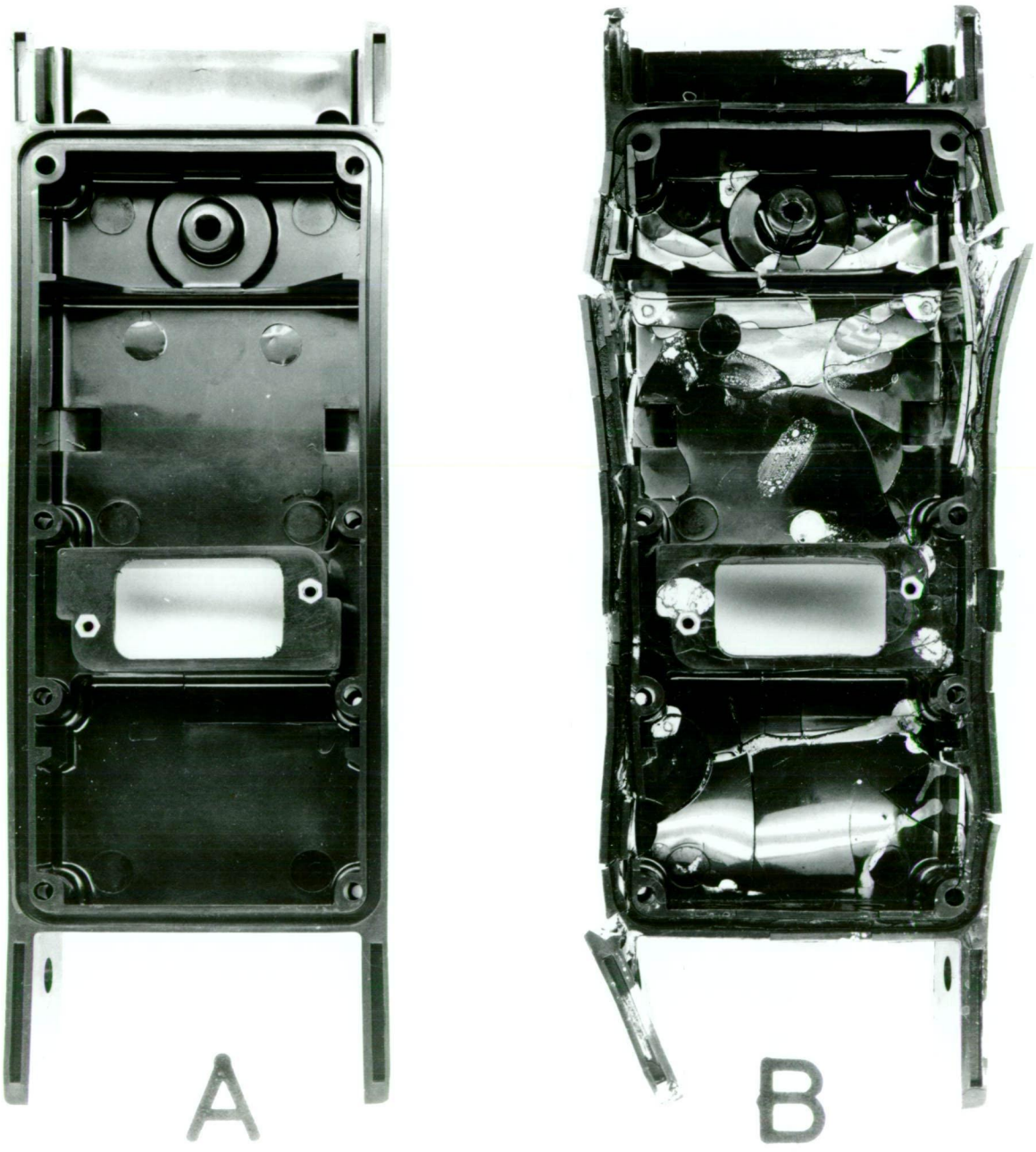

Appendix 15c. Nylon 6, Telephone Set K case moulding (length 230 mm). A, untreated; B, treated with 80% zinc chloride solution at room temperature for 24h (mag., 0.70).

UNCLASSIFIED

APPENDIX 15d

DEPARTMENT OF SUPPLY
AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
DEFENCE STANDARDS LABORATORIES

REPORT 300

CASE AND SEAL MATERIALS FOR TELEPHONE SET K

PART 1 : CASE MATERIALS
PART 11 : SEAL MATERIALS

P. DUNN, T. LIGGINS* and T. NORRIS**

SUMMARY

Failures in telephone cases made from nylon 6 have been investigated. The failures varied in form from fine cracks in the surface, to serious delamination of the moulding, or to complete disintegration. These stress cracking failures were initiated by zinc chloride present in electrolyte that had leaked from discharged dry cells. The rate and degree of cracking by zinc chloride solutions was dependent on the temperature, the concentration of zinc chloride, the water content of the nylon and the level of stress in the mouldings. Telephone cases moulded from nylon 11 (polyundecanoamide) are resistant to attack by zinc chloride solutions.

Rubber seals for Telephone Set K have been examined and it has been shown that most can be replaced by ethylene-propylene copolymer valcanizates. Rubbers of two different hardness grades are adequate.

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DECEMBER, 1967

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4. Recommended Tests on Small Components.

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Appendix 15e. Stress cracking of a moulded nylon 6 safety glass frame by 80% zinc chloride solution. Conditions: temperature, 22 °C; time to crack initiation, 12 min; time to fracture, 45 min. Top: original frame; middle - drops of solution applied at points A-J; bottom-fractured frame (mag., X0.90).

APPENDIX 16 MECHANISM OF STRESS CRACKING OF NYLON

16a The Stress Cracking of Polyamides by Metal Salts. Part I. Metal Halides.
P. DUNN and G.F. SANSOM.
J. Appl. Polym. Sci., 13, 1641-1655 (1969) 16.2 - 16.16

16b Stress Cracking of Nylon by Zinc Chloride (1968). 16.17

16c Stress Cracking of Nylon by Zinc Chloride (1978). 16.18

16d Stress Cracking of Nylon by Chromic Chloride - Enlargement of Cracking Pattern. 16.19

16e The Stress Cracking of Polyamides by Metal Salts. Part II. Mechanism of Cracking.
P. DUNN and G.F. SANSOM.
J. Appl. Polym. Sci., 13, 1657-1672 (1969). 16.20 - 16.35

16f The Stress Cracking of Polyamides by Metal Salts. Part III. Metal Thiocyanates.
P. DUNN and G.F. SANSOM.
J. Appl. Polym. Sci., 13, 1673-1688 (1969). 16.36 - 16.51

16g The Stress Cracking of Polyamides by Metal Salts. Part IV. Metal Nitrates.
P. DUNN and G.F. SANSOM.
J. Appl. Polym. Sci., 14, 1799-1806 (1970). 16.52 - 16.59

JOURNAL OF APPLIED POLYMER SCIENCE VOL. 13, PP. 1641–1655 (1969)

The Stress Cracking of Polyamides by Metal Salts. Part I. Metal Halides

P. DUNN and G. F. SANSOM, *Australian Defence Scientific Service, Department of Supply Defence Standards Laboratories, Melbourne, Australia*

Synopsis

The stress cracking of polyamides (nylons) by a number of metal salts, in aqueous and nonaqueous solutions, has been investigated. Many metal halides and halide-like salts were found to be active stress-cracking agents, while metal acetates and sulfates were inactive. Zinc chloride was found to be most active, and its activity was compared with other metal halides. Using a recording tensometer, time to crack initiation, time to crack-through and time to rupture were determined. These parameters were found to be dependent on temperature, moisture content of the nylon, concentration of the cracking agent and level of stress. High values of all these factors favored rapid cracking. Cracking parameters were shown to be mainly independent of the surface geometry of the nylon and the hydrogen ion concentration of the cracking agent. Metal halides did not appear to cause any chain scission in the nylon and stress cracking was not due to hydrolysis or metal-ion catalysed hydrolysis.

INTRODUCTION

The cracking and delamination of nylon 6 and nylon 66 mouldings in the presence of aqueous zinc chloride solutions ranging in concentration from 20–80% weight/volume,[1] and also in the presence of zinc dust and hydrochloric acid[2] had been reported. Weiske[3] has described the stress cracking of dry nylons by a number of solvents and the action of methanolic solutions of calcium chloride. Barmby and King[4] have shown that both silk and nylons are soluble in arsenic and antimony trichlorides with little apparent molecular chain degradation, and that silk precipitated from an aqueous lithium bromide solution is similar to silk precipitated from solution in antimony trichloride. Sarda and Peacock[5] have shown that lithium bromide and lithium and magnesium perchlorates in aqueous solution reduce the modulus properties of nylon 6 and 66 and also bring about modification of the infrared spectra of these polyamides. A comparison of the effects of a range of metal salts on polyamides has now been undertaken.

EXPERIMENTAL

Materials

Nylon 6 test specimens were cut from extruded nylon 6 sheet ("Trogamid" B; Dynamit-Nobel A.G., Troisdorf, Germany), as rectangular

strips 6 × 1 × 0.125 in. Dumbell tensile specimens, with neck dimensions 2 × 0.50 × 0.040 in. were stamped from nylon sheet using Die A, of ASTM-D412.[6] Other nylon specimens were in the form of injection moulded dumbells conforming to British Standard BS 2782.[7] The moulding compounds used were:

Nylon 6,	"Grilon" A25G, Natural (Emser Werke A.G., Switzerland)
Nylon 66,	"Maranyl" A100, Natural (Imperial Chemical Industries Ltd., England)
Nylon 610,	"Maranyl" B1001C, Natural (Imperial Chemical Industries Ltd., England)
Nylon 11,	"Rilsan" BMNO, Natural (Société Organico, France)

Where possible the metal salts employed were analytical grade and were used without further purification. All solvents were laboratory grade and were purified by distillation and then dried. Distilled water was used throughout.

Measurement of Stress Cracking Parameters

To assess the activity of metal salts, test specimens of nylon 6 were stressed horizontally between the grips of a Hounsfield tensometer at stress levels of 2000 and 4000 psi, and single drops of saturated solutions of

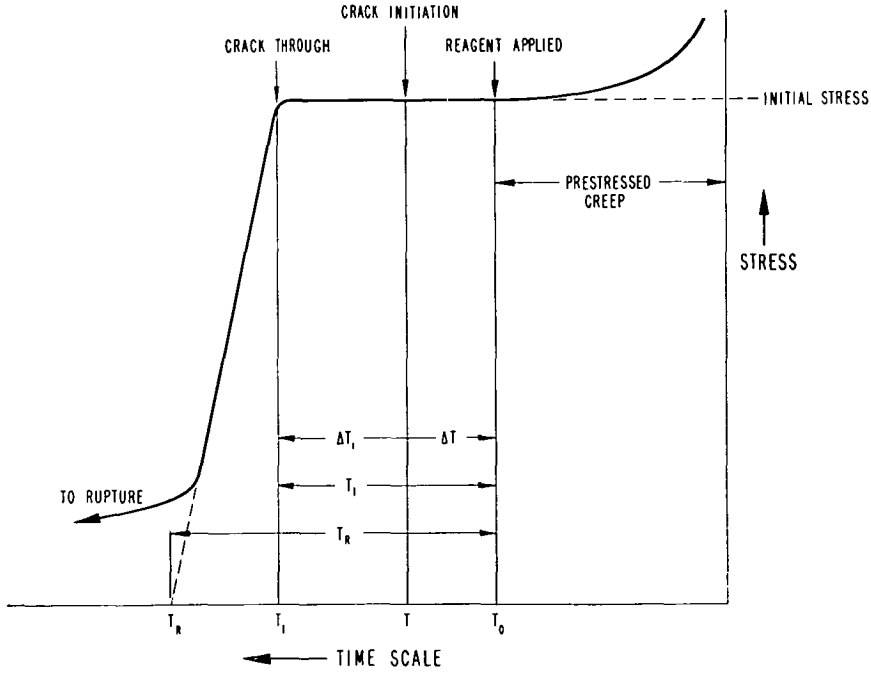


Fig. 1. Schematic stress-time curve.

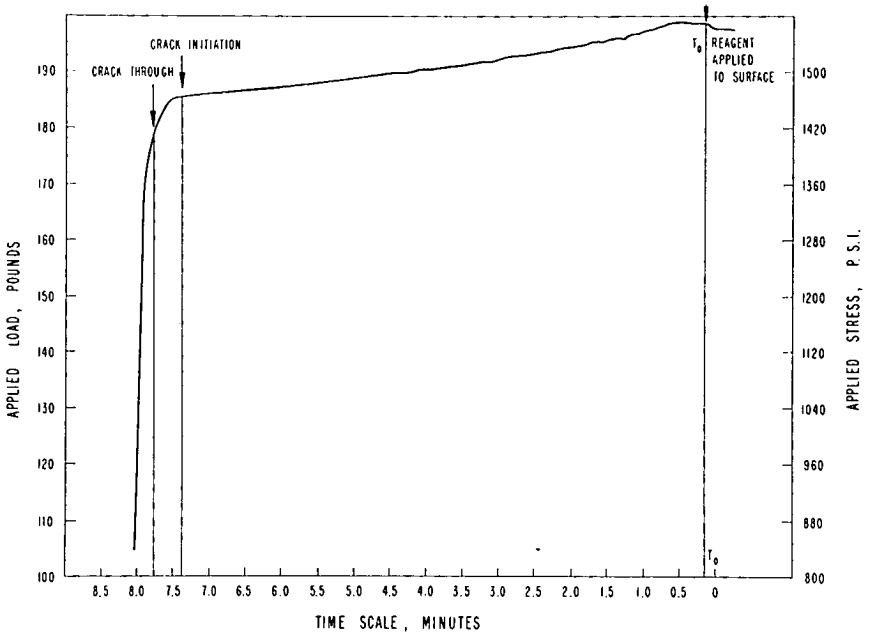


Fig. 2. Typical experimental stress-time curve for nylon 6 (moisture content, 3.5%) stress cracked by saturated methanolic $ZnCl_2$ solution, at 21°C.

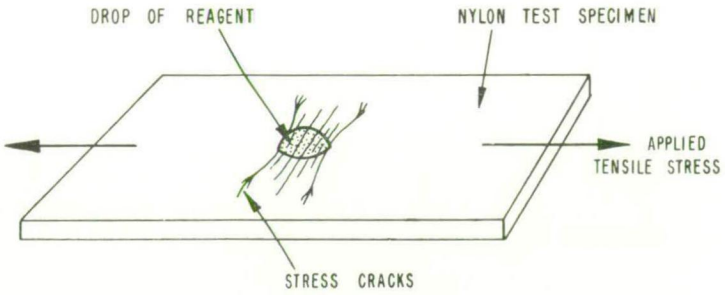
the reagent applied to the surfaces. The initiation of cracking within 48 hr was taken as proof of stress cracking activity. Initially a simple separation into highly active, active, weakly active and inactive categories was carried out on the basis of whether total rupture of the specimen occurred rapidly, within the period of the test, failed to occur even though crack initiation took place, or no cracking occurred. Some reagents failed to cause cracking but caused swelling of the nylon and this was always described as weak activity.

To quantitatively investigate the activity of the metal salts, stressed specimens at constant strain were treated with the reagent and the stress, which decreased as cracking took place, was continuously recorded. The stress was recorded by means of a Phillips pick up in contact with the spring beam of the tensometer; the output of the pick up was indicated on a Sargent model SRL variable speed recorder.

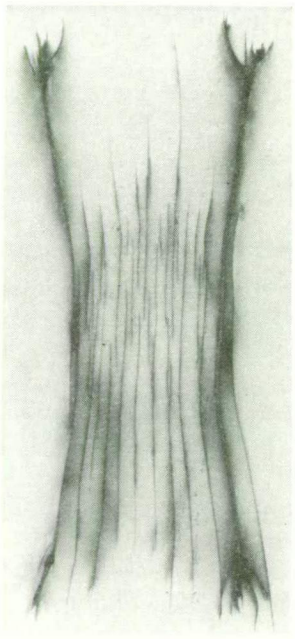
All specimens were prestressed and then allowed to relax under creep until the stress remained nearly constant before the reagent was applied to the surface. Thus, stress-time curves of the type shown schematically in Figure 1 were obtained. A typical curve for nylon 6 stress cracked by methanolic zinc chloride solution is shown in Figure 2 and a typical cracked specimen in Figure 3.

The cracking process was followed visually by observing the nylon surface through a mounted, moveable large magnifier, fitted with inbuilt fluorescent illumination. Initiation of cracking was detected using low

angle illumination and observation. A plane mirror sited under the specimens, together with low angle illumination, was used to observe when the crack appeared at the under surface.



(*a*)



(*b*)

Fig. 3. (*a*) Typical experimental procedure. (*b*) typical stress cracking: nylon 6 stress cracked by aqueous (80%) $ZnCl_2$ solution. The water soluble dye, Nigrosine G140, was added to the solution in order to indicate the stress cracking pattern. The initial stress was 2000 psi, and the test temperature, 21°C (× 4 magnifications).

From visual observation, and the stress-time curves, the following cracking parameters were obtained.

Crack Initiation Time (ΔT): the crack initiation time is defined as the period between application of a drop of the test reagent and the first visible

cracking of the surface of the test specimen. Without observation, this parameter cannot be derived from the stress-time curve.

Crack-through Time (T_1): the crack-through time is defined as the period between application of the test reagent to the upper surface of the test specimen and the first appearance of visible cracking on the underside of the specimen. In practice it is found that this corresponds to the time interval T_1–T_0 shown on the typical stress-time curve. After crack-through the stress decreases rapidly.

Time to Rupture (T_R): the time to rupture is defined as the period from initial application of the test reagent to the time of final rupture of the specimen (zero stress). In some cases where the stress, after reaching a low value, failed to decrease at the previous rate an extrapolated value for T_R (Fig. 1) was used.

Crack-through Propagation Period (ΔT_1): the crack-through propagation period is defined as the period elapsed between crack initiation and crack through, that is $\Delta T_1 = T_1 - \Delta T$. From this period the crack propagation rate, K, may be calculated (section G). This represents a useful semiquantitative method of ranking the activity of various cracking agents under the test conditions. Although numerical values are employed, emphasis should only be placed on the order of magnitude.

RESULTS

A. Qualitative Assessment of Stress Cracking Agents

The activities of metal halides on stressed nylon 6 are shown in Table I. Certain metal halides and halide-like salts were active stress cracking agents in aqueous solution. Other soluble salts such as sulfates and acetates were inactive. Some agents, such as vanadium chloride and chloroauric acid were weakly active in aqueous solution, and caused surface swelling and softening of the stressed nylon.

In saturated methanolic solution many of the metal halides found to be active in aqueous solution had their activity enhanced, while others such as nickel$_{II}$ chloride, manganese$_{II}$ chloride and calcium chloride which were inactive in aqueous solution became active. Only two salts, aluminium chloride and mercuric chloride, which were active in aqueous solution were found to be inactive in methanolic solution.

Solutions of lithium chloride, cobalt$_{II}$ chloride and zinc chloride in acetone, ethanol, n-propanol, and amyl alcohol were also active cracking agents, but solutions of these salts in dimethyl sulfoxide and ethylene glycol were inactive. None of these solvents showed any stress cracking activity.

B. Reproducibility of Results

For any given set of conditions the cracking parameters are not completely reproducible. However a probability of crack initiation, crack-

through and rupture within certain time limits can be determined. Generally time to rupture (T_R) was more reproducible than time of crack-through (T_1). Typical results showing the probability of rupture with zinc chloride solutions are shown in Table II.

TABLE I
Activity of Metal Halides on Stressed Nylon 6

	Activity in aqueous solution (saturated)		Activity in methanolic solution (saturated)	
	At 4000 psi stress	At 2000 psi stress	At 4000 psi stress	At 2000 psi stress
LiCl	+	−	++	++
LiBr	+++	+++	+++	+++
LiI	−	−	++	++
$LiNO_3$	−	−	+	+
NaCl	−	−	−	−
KCl	−	−	−	−
NH_4Cl	−	−	−	−
$CuCl_2$	+	−	+	−
Chloroauric acid	+	−	0	0
$MgCl_2$	+	−	+	+
$CaCl_2$	−	−	++	++
$MgClO_4$	+++	+++	0	0
$SrCl_2$	−	−	−	−
$BaCl_2$	−	−	−	−
BaI_2	−	−	++	++
$BaBr_2$	−	−	+	+
$ZnCl_2$	+++	+++	+++	+++
ZnI_2	+++	+++	+++	+++
$CdCl_2$	−	−	−	−
$CdBr_2$	−	−	+	+
CdI_2	+	−	+	−
$HgCl_2$	+	−	−	−
$AlCl_3$	+	−	−	−
$InCl_3$	++	++	++	++
YCl_3	+	0	0	0
Rare earth chlorides[a]	++	0	0	0
$SnCl_2$	−	−	−	−
$PbCl_2$	−	−	−	−
VCl_2	+	+	++	0
$CrCl_3$	++	−	++	0
$FeCl_3$	++	−	++	+
$CoCl_2$	++	++	++	++
$NiCl_2$	−	−	+	0
$PtCl_4$	++	++	0	0
$PdCl_2$	+	−	0	0

Key to Table I: +++, highly active; ++, active; +, weakly active; −, inactive and 0 not tested.

[a] The chlorides of the following rare earths were used: yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium, yerbium, dysprosium, holmium, erbium, europium, ytterbium.

TABLE II
Typical Times to Rupture for Zinc Chloride Solutions on Stressed Nylon 6[a]

Probability of rupture	Time to rupture, min	
	Aqueous 80% $ZnCl_2$ solution	Saturated methanolic solution
90% of specimens ruptured	Within 21	Within 10
60% of specimens ruptured	Within 14.5	Within 4.2
50% of specimens ruptured	Within 12.5	Within 3.5
40% of specimens ruptured	Within 12	Within 2.75
20% of specimens ruptured	Within 10.8	Within 2.4
10% of specimens ruptured	Within 9.5	Within 1.5

[a] Conditions: Nylon 6 specimens, 3.5% water content, initial stress 2500 psi, 21°C.

C. Effect of Concentration

With zinc chloride solutions ranging in concentration from 50–80% (w/v), stress cracking data indicated that the concentration did not greatly affect the time to crack initiation. However, with further decreasing concentration the time to rupture increased and the crack propagation rate decreased. Below 30% concentration, crack initiation was extremely slow.

D. Effect of Moisture Content of the Nylon

The moisture content of nylon 6 had a marked effect on the rate of cracking. Dry nylon 6 specimens under stress (3600 psi) showed no crack initiation within 4300 min while samples conditioned to 2.5–3.5% water content were completely ruptured in 20–60 min, and samples conditioned to a water content of about 10% were ruptured within 8 min.

Investigation of the effect of other conditioning agents for nylon, showed that water alone was not essential to the cracking process. Nylons conditioned in methanol, iso-propanol, acetone, ethylene glycol, or even water emulsifiable oil, were all susceptible to stress cracking by aqueous and methanolic solutions of metal salts (Table III).

TABLE III
Effect of Conditioning[a] Agent on Stress Cracking[b] of Conditioned Nylon 6 Specimens

Cracking agent	Times to crack initiation, sec						Time to rupture, sec					
	A	B	C	D	E	F	A	B	C	D	E	F
80% aqueous $ZnCl_2$	20	5	60	120	35	15	70	40	105	170	70	85
Saturated methanolic $ZnCl_2$	30	4	4	4	23	3	40	6	7	6	27	6

[a] Conditioning: Dry samples were conditioned by immersion, at room temperature, for 1 week in: A, distilled water; B, methanol; C, isopropanol; D, acetone; E, ethylene glycol; and F, water emulsifiable oil.

[b] Stress conditions: 2500 psi at room temperature.

As shown in Table III, saturated methanolic zinc chloride was a more active cracking agent than 80% zinc chloride solution, irrespective of the conditioning agent used. Samples conditioned with nonaqueous agents were more rapidly attacked by methanolic zinc chloride than samples conditioned with water.

Dry nylon or nylons with low equilibrium moisture content, such as nylon 11, were resistant to stress cracking by solutions of metal halides. Nylon 11 specimens however, conditioned for one week in methanol and then stressed at 2500 psi, cracked after 24 hr in contact with 80% zinc chloride solution, and after 1 min in contact with saturated methanolic zinc chloride. Nylon 11 specimens conditioned in a similar manner in distilled water and tested under the same stress conditions failed to show crack initiation with either reagent.

E. Effect of Temperature

Temperature has a marked effect on the rate of cracking of nylons by aqueous zinc chloride. Stressed nylon 6 specimens (water content, 3.5%) take greater than 250 min to crack-through at 3°C compared with 20–24 min at 21°C and 2–19 min at 27°C. Hot aqueous zinc chloride solutions (80°C) caused rapid cracking in stressed specimens.

F. Effect of Surface Conditions

Stressed nylon specimens with surfaces prepared by flame polishing, abrasion with course and fine emery, and notched both parallel and at right angles to the applied stress were shown to exhibit similar stress cracking parameters.

Specimens were tested with varying areas of contact between the stress cracking agent and the nylon surface. With the nylon cracking agent air interface unrestricted and the contact area between the cracking agent and the nylon determined only by drop size (as determined by the quantity of cracking agent applied) it was found that quantity and/or area of contact were not major factors in determining the rate of crack initiation. However, they could be important factors in determining the rate of crack propagation from initiation to crack through. For most determinations, drops of cracking agent were applied to the nylon surface with a micrometer syringe.

G. Comparison of Activity

As shown in Table IV aqueous zinc iodide, zinc chloride and lithium bromide at similar concentrations show the same order of activity.

Saturated aqueous solutions of cobalt$_{II}$ chloride were slower in action. The comparative activity of a range of lithium salts in both water and methanol is given in Table V.

Other metal halides were active in aqueous solution, in the order: $CoCl_2$, rare earth chlorides, $PtCl_4$, $CrCl_3$, $FeCl_3$, $HgCl_2$, $AlCl_3$, LiCl, $MgCl_2$. In

TABLE IV
Stress Cracking Activity of Aqueous Zinc Chloride and Zinc Iodide

Initial stress, psi	Time to crack-through, min at 21°C		
	$ZnCl_2$[a]	ZnI_2[a]	LiBr[a]
1400	36.5	75.5	—
2000	23.0	38.0	27.0
2500	8.2	12.3	—
3300	5.0	6.5	—
4300	3.4	4.0	—

[a] Solution concentration, 80% (w/v).

TABLE V
Stress Cracking Activity of Lithium Salts

Solution (saturated)	Time to crack initiation, min	Time to rupture, min
LiCl in water	>3000	[b]
LiCl in methanol	0.5	60
LiBr in water	10	23
LiBr in methanol	3	6
LiI in water	>1500[a]	[a]
LiI in methanol	400	405
Li acetate in water	>1500[a]	[a]
Li acetate in methanol	>1500[a]	[a]
Li nitrate in water	>1500[a]	[a]
Li nitrate in methanol	Approx. 1400	3000

[a] No crack initiation occurred.
[b] Crack initiation occurred very slowly.
Conditions: Nylon 6 specimens, 3.5% water content, initial stress 2000 psi, 21°C.

methanolic solution, activity of these salts was greatly enhanced. Methanolic solutions of $NiCl_2$, $MnCl_2$, and $CaCl_2$ also cause cracking of stressed nylons.

The comparative activity of stress cracking agents was assessed by determination of the rate of crack propagation through the nylon specimen.

The crack propagation rate (K), is defined by,

$$K = \frac{t}{T_1 - \Delta T}$$

where

t = thickness of the specimen
T_1 = period of crack-through
ΔT = period of crack initiation

Crack propagation rates for solutions of zinc, lithium, cobalt, and calcium chlorides on stressed nylon 6, as shown in Table VI, indicated that methanolic zinc chloride is the most active agent. The stress cracking activity of metal halides was also determined using a dynamic rupture technique in

TABLE VI
Crack Propagation Rates of Metal Halide Solutions[a]

Solution	Number of determination	Crack propagation rate (K), in. per min		
		$K_{max}{}^{m}$	$K_{min}{}^{m}$	K_{mean}
Aqueous $ZnCl_2$, 80%	16	0.028	0.005	0.010
Saturated methanolic $ZnCl_2$	10	0.059	0.010	0.030
Saturated methanolic LiCl	2	0.002	0.002	0.002
Saturated methanolic $CoCl_2$	2	0.001	0.001	0.001
Saturated methanolic $CaCl_2$	4	0.0005	0.0005	0.0005

[a] Conditions: Nylon 6 specimens, 3.5% water content, initial stress 2000 psi, 21°C. The specimens were 0.125 in. thick. A smaller number of determinations was carried out for less active agents because of the slower cracking rate. Where cracking occurred more slowly, results were much more reproducible. However, results are still only quoted to one significant figure.

which nylon 6 test specimens were extended at a rate of 0.0625 in./min and the load continuously recorded while in contact with the cracking agent. The time to rupture (T_R) was determined and an activity factor (A) then derived from the equation $A = 1/T_R \cdot (1)/(M)$
where

T_R = time to rupture of specimen
M = molar concentration of cracking solution

The activity factors for some cracking agent solutions, as shown in Table VII, show that methanolic zinc chloride is the most active agent followed, in order, by methanolic $cobalt_{II}$ chloride, aqueous zinc chloride, methanolic calcium chloride and methanolic lithium chloride.

TABLE VII
Stress Cracking Activity of Metal Halides under Dynamic Stress Conditions[a]

Agent	Number of determinations	Average time to rupture, min	Activity factor, min^{-1} $mole^{-1}$
Aqueous $ZnCl_2$, 80%	2	11.5	0.015
Aqueous $ZnCl_2$, 40%	1	12.35	0.028
Saturated methanolic $ZnCl_2$	4	5.55	0.041
Saturated methanolic LiCl	3	19.7	0.005
Saturated methanolic $CaCl_2$	4	42.0	0.011
Saturated methanolic $CoCl_2$	3	19.43	0.032

[a] Conditions: Nylon 6 specimens, 3.5% water content, 21°C. The specimens were 0.125 in. thick.

H. Effect of Stress

As with all other stress cracking phenomena, the initiation of cracking, rate of crack-through, rate of crack propagation and time to rupture in the cracking of nylon by metal halide solutions are stress dependent quantities.

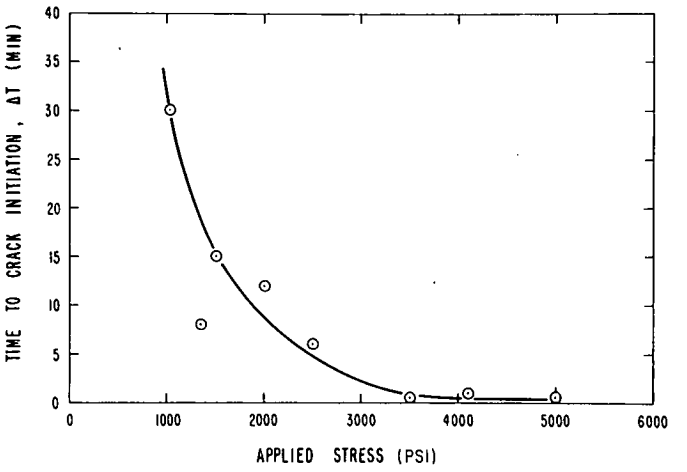


Fig. 4. Effect of stress on time to crack initiation for nylon 6—stress cracked by 80% aqueous $ZnCl_2$ solution, at 21°C.

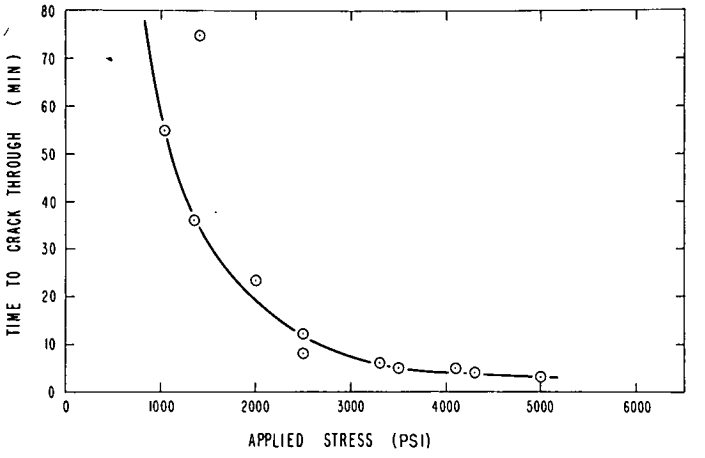


Fig. 5. Effect of stress on time to crack-through for nylon 6—stress cracked by 80% aqueous $ZnCl_2$, at 21°C.

This has been demonstrated for the cracking of nylon 6 by both aqueous and methanolic zinc chloride.

The effect of stress in nylon 6, when treated with 80% aqueous zinc chloride, on the crack initiation time, on the crack-through time and on the time to rupture is shown in Figures 4, 5, and 6, respectively. The effect of stress in nylon 6, when treated with methanolic zinc chloride, on the crack-through time is shown in Figure 7.

These results indicate that a minimum stress level in nylon 6 of about 700–800 psi is required before stress cracking can be initiated by solutions of metal halides. Since injection moulded nylon components are also

rapidly cracked by solutions of zinc chloride[1] it is most probable that these components have internal stresses of a high order. The level of internal stress in nylon mouldings can be estimated by determination of the time to rupture when in contact with zinc chloride solution under standard conditions.

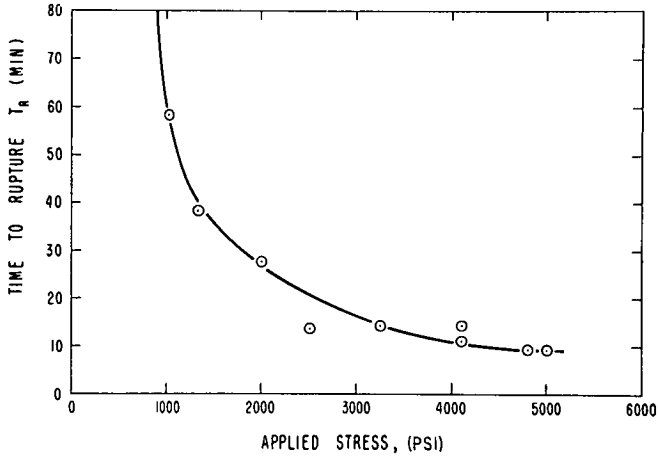


Fig. 6. Effect of stress on time to rupture for nylon 6, stress cracked by 80% aqueous $ZnCl_2$, at 21°C.

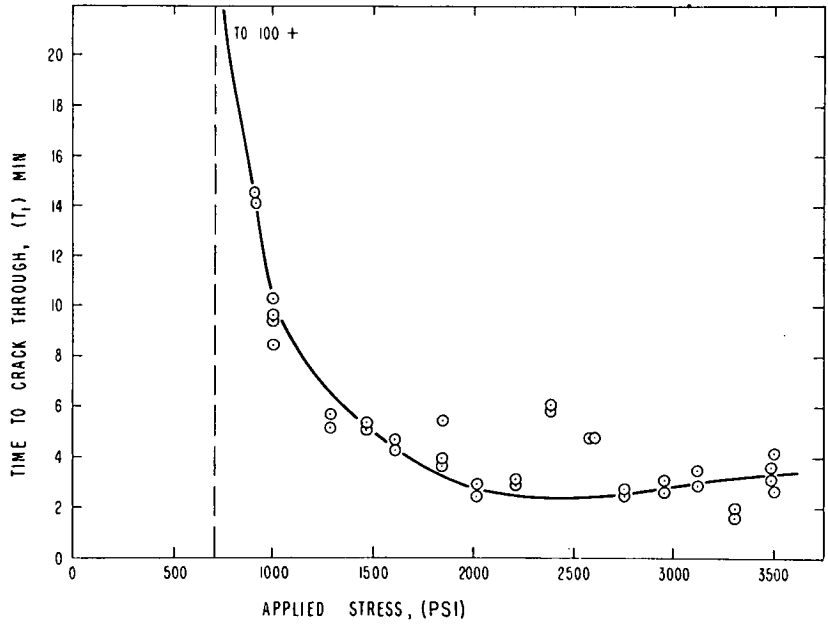


Fig. 7. Effect of stress on time to crack-through for nylon 6, stress cracked by saturated methanolic $ZnCl_2$, at 21°C.

Effect of Zinc Chloride on Unstressed Nylon

Unstressed, injection moulded, dry nylon 6 tensile test specimens were conditioned for various periods in distilled water and in 40% aqueous zinc chloride, after which they were washed clean and wiped dry. The tensile strengths of the specimens treated by these alternative conditioning agents were then determined and compared. The results (Table VIII) showed only minor differences between the water conditioned specimens and the zinc chloride conditioned specimens, and indicated that no embrittlement of the unstressed mouldings had occurred in the zinc chloride solution.

TABLE VIII
Effect of Zinc Chloride on Unstressed Nylon 6

Period of conditioning, days	Moisture content, % (approx)	Tensile yield strength, psi	
		Conditioned in water	Conditioned in 40% zinc chloride solution
Nil(Controls)		7000, 6850, 6720, 6700	
1.25	2	6020, 5800, 6120	6360, 6360, 6440
8	4	4150, 4150, 4160	4020, 3900, 3800
17	6	3800, 3860, 3870	3780, 3720, 3820
31	8	3670, 3640, 3620	3470, 3460, 3410
52	10	3320, 3420, 3320	3250, 3210, 3220
80	Saturated	3220, 3400, 3460	3220, 3120, 3300

Viscosity measurements of nylon 6 in formic acid solution showed that the intrinsic viscosity did not decrease, on standing, in the presence of zinc chloride, indicating that reduction of molecular weight due to chain scission did not occur. However, it was shown that the viscosity of nylon in formic acid solution was reduced in the presence of zinc chloride. Some modification of the polymer structure in the presence of zinc chloride had probably occurred.

DISCUSSION

Stuart, Markowski, and Jeschke[8] have described a mechanism of environmental stress cracking by solvents or other liquids capable of wetting the surface of polymeric materials. These are often capable of being absorbed, cause swelling of the polymer and induce critical localized stresses which cause fine cracks to appear at surface flaws. This is more likely to occur where such flaws are associated with boundaries between separate crystalline regions in the polymer. They also indicate that factors such as instantaneous increase in local notch stresses, "microplasticization" and also gross plasticization of the polymer due to the cracking agent are all important factors in the stress cracking process.

Methanolic and aqueous solutions of the metal halides are usually viscous and surface wetting does not occur readily. Also in most cases crack

initiation does not occur in the area under the droplet but at the nylon-reagent-air interface. The presence of gross surface imperfections does not appear to markedly affect the rate of crack initiation.

Microplasticization and gross plasticization occurs, since all of the cracking agents are effective swelling agents for nylon. The presence of water or other nonaqueous conditioning agents, which are also swelling agents, in the nylon is essential for stress cracking by metal halides to occur. This result for nylon is at variance with the effects of prior conditioning with swelling agents on the stress cracking of polythene described by Stuart et al.[8]

The presence of a metal halide in solution is essential for this type of stress cracking. It would appear that the role of the solvent, and the conditioning agent, is not only to act as a swelling agent, but also to provide a transport medium by which the metal halide can be absorbed into the nylon. We believe the absorbed metal halide mainly promotes stress cracking by chemical means.

TABLE IX
The Effect of pH on the Stress Cracking of Nylon 6[b]

Solution	pH	Crack initiation time, min	Rupture time, min
$ZnCl_2$ solution, (35%)	4.29	1	80–140
$ZnCl_2$ solution, (18%) adjusted with HCl	4.89	>1500	—
$ZnCl_2$ solution, (4.5%) adjusted with HCl	1.45	>1500	—
Hydrochloric acid (12 N)	0	nil[a]	nil[a]

[a] Extensive swelling and softening.

[b] Conditions: nylon 6 specimens, 3.5% water content, initial stress 2000 psi, temperature 21°C.

Weiske[3] has described the stress cracking of dry nylons by polar solvents and in this case a simple physical mechanism is involved. He has also described the cracking of nylons by dilute mineral acids. Hydrochloric acid (5%) was reported to cause cracking in conditioned nylon 6 and 6.6 within 2–3 months and 2% hydrochloric acid caused embrittlement in one year. The mechanism proposed was one of simple hydrolysis, with the rate of crack initiation being a function of hydrogen ion concentration.

We found solutions of hydrochloric acid of equivalent hydrogen ion concentration to active zinc chloride solutions (80% $ZnCl_2$, pH 0; 20% $ZnCl_2$, pH 5.2) would not cause rapid stress cracking of nylon. Dilute solutions of zinc chloride, adjusted by the addition of hydrochloric acid to a hydrogen ion concentration equivalent to that of the more concentrated active solutions, were very slow cracking agents.

Results as shown in Table IX indicate that the stress cracking of nylon 6 by metal halide solutions is not a function of the hydrogen ion concentra-

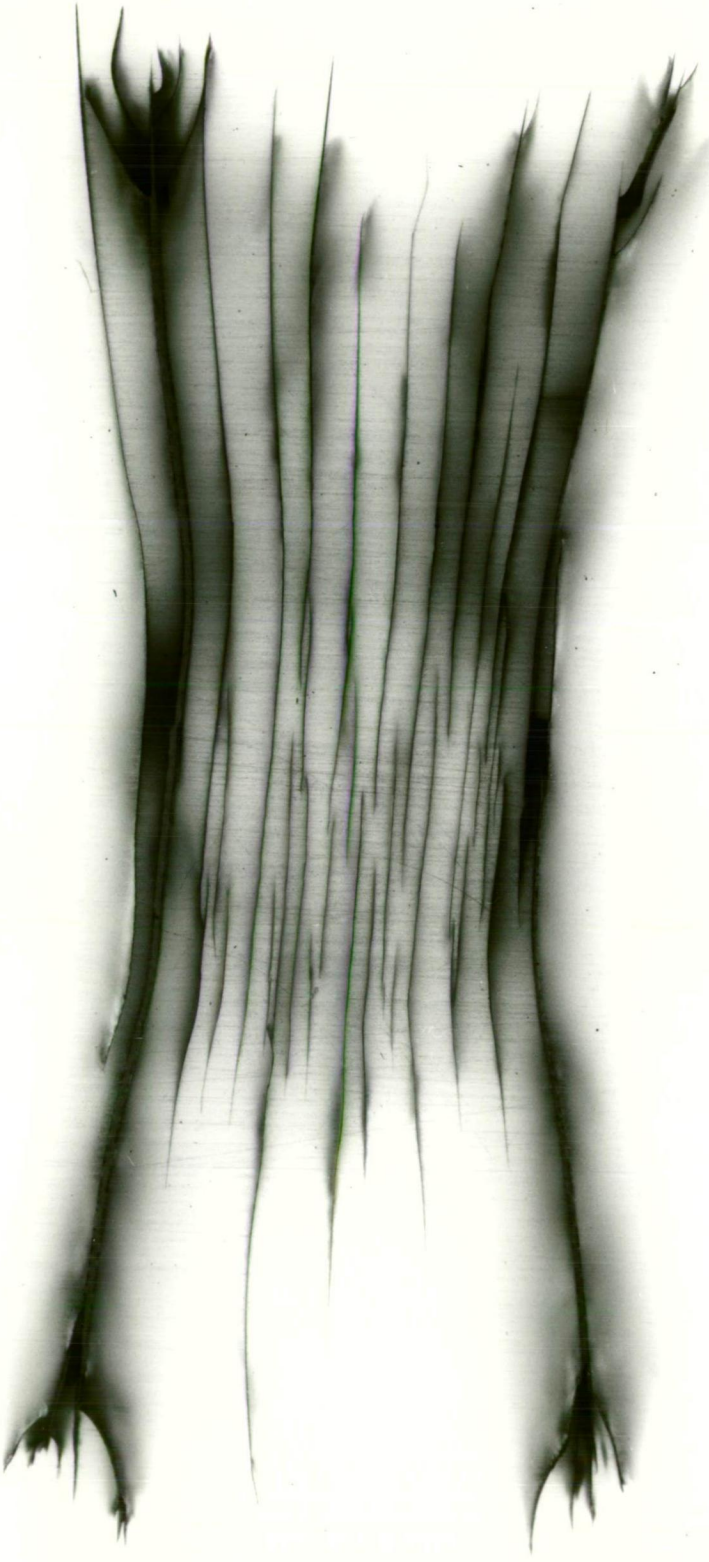
tion, and it is unlikely that the mechanism is one of hydrolysis or metal-ion catalysed hydrolysis.

We believe the stress cracking mechanism involves reactions between the metal halide and the nylon. This has been investigated using infrared techniques and is described in Parts II and III.

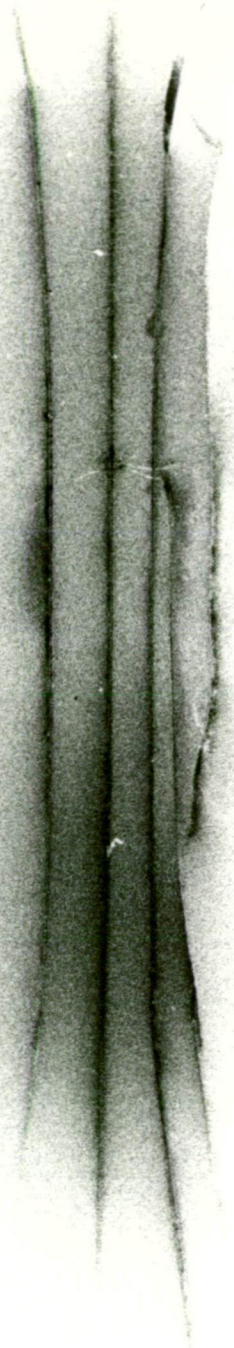
References

1. P. Dunn, A. J. C. Hall, and T. Norris, *Nature*, **195**, 1092 (1962).
2. M. Ensanian, *Nature*, **193**, 161 (1962).
3. C. D. Weiske, *Kunststoffe*, **54**, 626 (1964).
4. D. S. Barmby and G. King, *Proc. Intern. Wool Textiles Res. Conf.* (Australia), **B-139** (1955).
5. G. Sarda and N. Peacock, *Nature*, **200**, 67 (1963).
6. ASTM: D412-66, *Tension Testing of Vulcanized Rubber*, American Society for Testing and Materials, 1968, Part 27, Philadelphia, Pa.
7. British Standard, B.S. 2782, *Methods of Testing Plastics. Part 3. Mechanical Properties*, British Standards Institution, 1965, p. 135. Method 301D, Figure 301.9, London.
8. H. A. Stuart, G. Markowski, and D. Jeschke, *Kunststoffe*, **54**, 618 (1964).

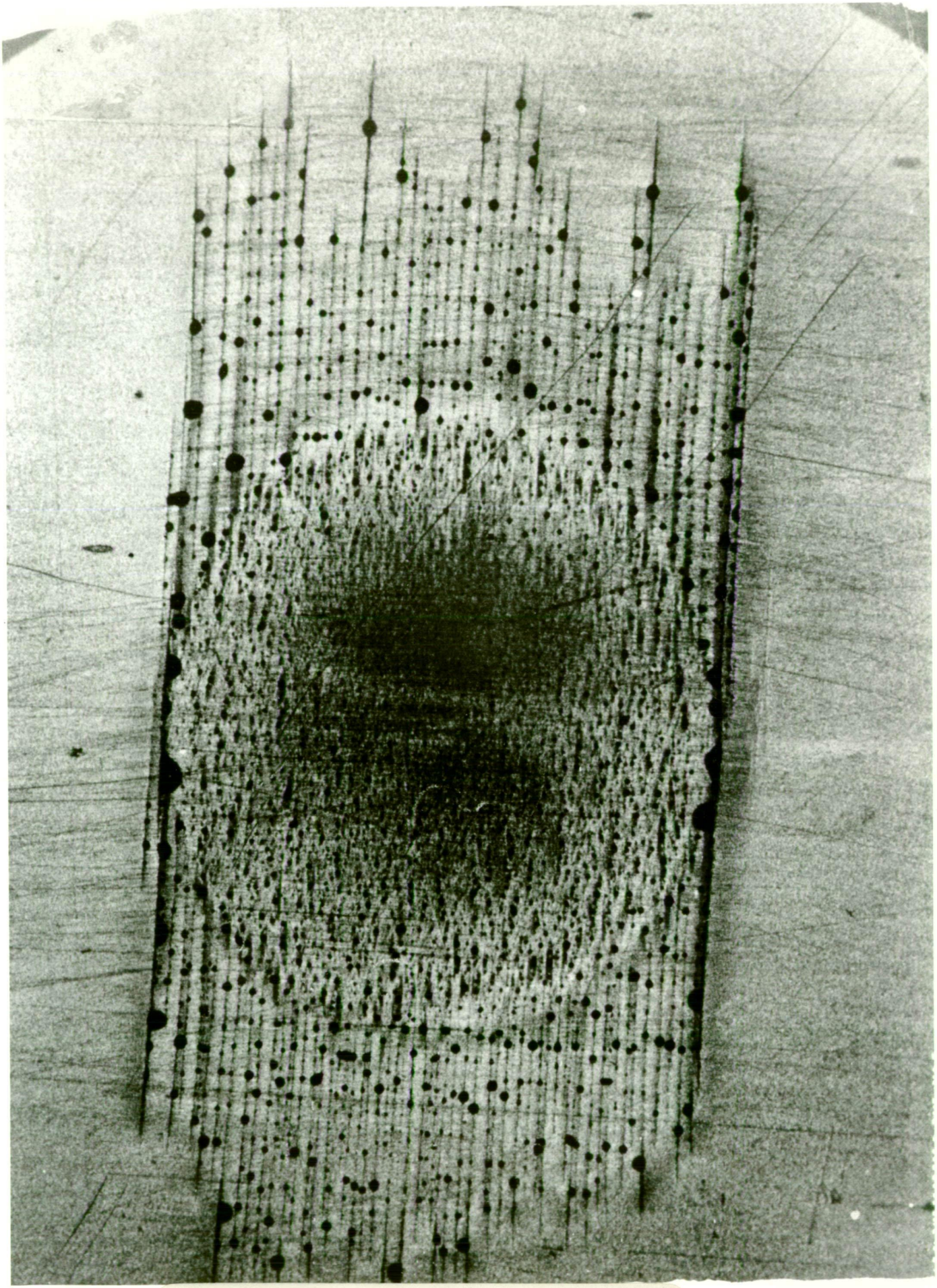
Received January 31, 1969



Appendix 16b. Stress cracking of nylon 6 by 80% zinc chloride solution. Conditions: temperature, 21°C; stress, 2000 psi; time to observed cracking, 30 min (mag., X10). For ease of observation the solution was coloured with Nigrosine G140.



Appendix 16c. Stress cracking of nylon 6 by 80% zinc chloride solution. Conditions: temperature, 22°C; water content of nylon, 3.3%; stress, 1700 psi; time to observed cracking, 55 min. (mag., X15). For ease of observation the solution was coloured with Disulphine Blue CN.



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Appendix 16d. Stress cracking of nylon 6 by saturated chromic chloride solution. Conditions: temperature, 22 °C; water content of nylon, 3.3%; stress, 4000 psi; time to observed cracking, 4h. (mag., X16).

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The Stress Cracking of Polyamides by Metal Salts. Part II. Mechanism of Cracking

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Synopsis

The action of metal halides on polyamide (nylon 6) and secondary amide model compounds has been investigated, using infrared and NMR techniques. Metal halides, which are active stress cracking agents for polyamides, induce characteristic changes in the spectra of both nylon 6 and the model compounds. Two types of changes were observed, depending on the metal halide involved, and on this basis the metal halides have been classified as Type I or Type II. The spectral changes appear to be due to the formation of complexes between the amide group and the metal halide, and structures for these complexes are proposed. Type I metal halides, such as zinc, cobalt$_{II}$, copper$_{II}$ and manganese$_{II}$ chlorides, form complexes in which the metal atom is coordinately bonded to the carbonyl oxygen atom of the amide group. These agents cause stress cracking by interference with the hydrogen bonding in the polyamide. Type II metal halides, such as lithium, calcium and magnesium chlorides and lithium bromide in solution form proton donating, solvated, species which act as direct solvents for nylon 6 in a manner similar to phenols and formic acid. Type II agents appear to cause simple solvent cracking.

INTRODUCTION

In Part I,[1] the action of a number of metal halides, in both aqueous and methanolic solution, on polyamides (nylons) has been described. The mechanism of rupture does not appear to be one of simple hydrolysis or of metal catalysed hydrolysis. Concentrated solutions of metal halides actively promoted stress cracking but solutions of hydrochloric acid of the same or higher hydrogen ion concentration were inactive even in the presence of lower concentrations of active metal halides. Solutions of metal acetates and sulphates did not promote cracking. The chemical action of the stress cracking agents of nylon 6 films and model compounds, has now been investigated.

EXPERIMENTAL

Film Treatments

Nylon films, as controls, were prepared for infrared studies by biaxially stretching 0.001 in. thick extruded, blown, unplasticised nylon 6 film.

Treated films were produced by immersing samples of 0.001 in. thick film in solutions of active metal salts for various periods, after which the films were removed and excess solution removed from the surface of the nylon with absorbent paper. The films were then biaxially stretched over a 1.0 in. diameter open-ended cylindrical glass support and dried.

Cast films containing metal salts were also prepared. Addition of a methanolic solution of the metal salt to a formic acid solution of nylon 6 gave a mixed solution, from which films were cast onto an ultrathin polypropylene support film.

Model Compounds

N-ethyl acetamide was purified by distillation. ϵ-Caprolactam was purified by repeated recrystallization from cyclohexane and dried over phosphorus pentoxide to give a white crystalline product of mp, 67°C *N*-methyl-2-pyrrolidone was purified by distillation.

Preparation of Complexes

Complexes of *N*-ethyl acetamide and *N*-methyl-2-pyrrolidone with metal salts were prepared by addition of an acetone solution of the amide to a methanolic solution of the metal salt followed by evaporation under vacuum to a small volume. Repeated additions of dried petroleum ether, followed by evaporation, gave solid products with $cobalt_{II}$ chloride but viscous liquids or glasses with zinc chloride.

Complexes of ϵ-caprolactam and $cobalt_{II}$ chloride were prepared by dissolving the anhydrous chloride in molten ϵ-caprolactam under dry, CO_2-free nitrogen, until deep blue solutions were obtained. These solutions were then allowed to cool and solidify. No attempt was made to isolate the pure complexes from the solidified reaction mixtures, but care was taken to ensure that correct stoichiometric quantities were used.

Infrared Spectra

The infrared spectra of the treated nylon films, cast films and model compound reaction products were determined on a Beckman I.R. 8 or Perkin-Elmer 125 spectrophotometer. The spectra of the films were recorded directly, or in the case of some cast films, on an ultra-thin polypropylene support film. Spectra of the complexes were obtained on nujol mulls between NaCl plates, or in KBr disks.

NMR Spectra

The NMR spectra of the complexes were obtained in acetone solution, using a Varian HA-60-IL spectrometer.

RESULTS

Action of Metal Halides on Nylon 6 films

Immersion of nylon 6 films in reagent solutions for 30 min followed by mounting, washing and drying gave films with an opaqus appearance. The

infrared spectra of these films showed no gross changes from those of untreated films.

However, nylon 6 films treated with aqueous zinc chloride solutions or methanolic solutions of other stress cracking metal halides, and dried,

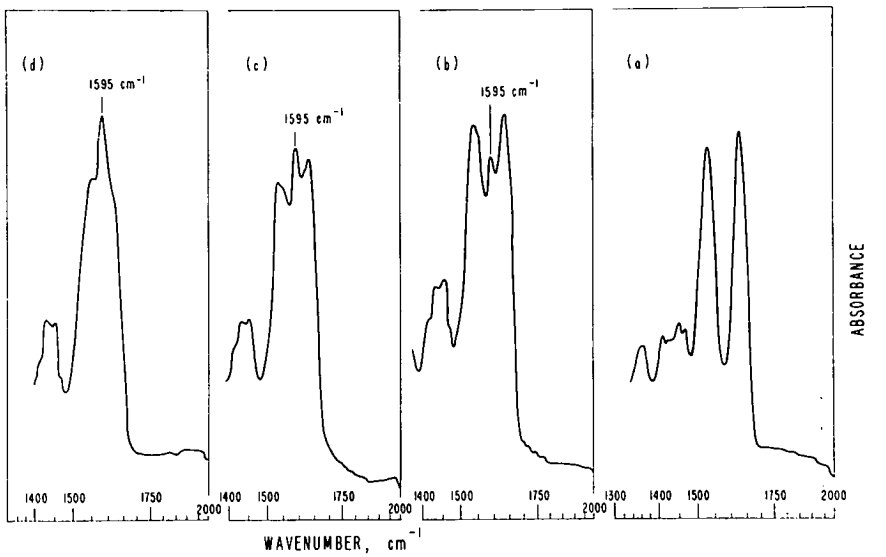

Fig. 1. Spectral changes in nylon 6 film treated with aqueous $ZnCl_2$ (80% w/v): amide I and amide II band region. (*a*) Untreated; (*b*) treated, 30 min.; (*c*) treated, 120 min.; (*d*) treated, 240 min.

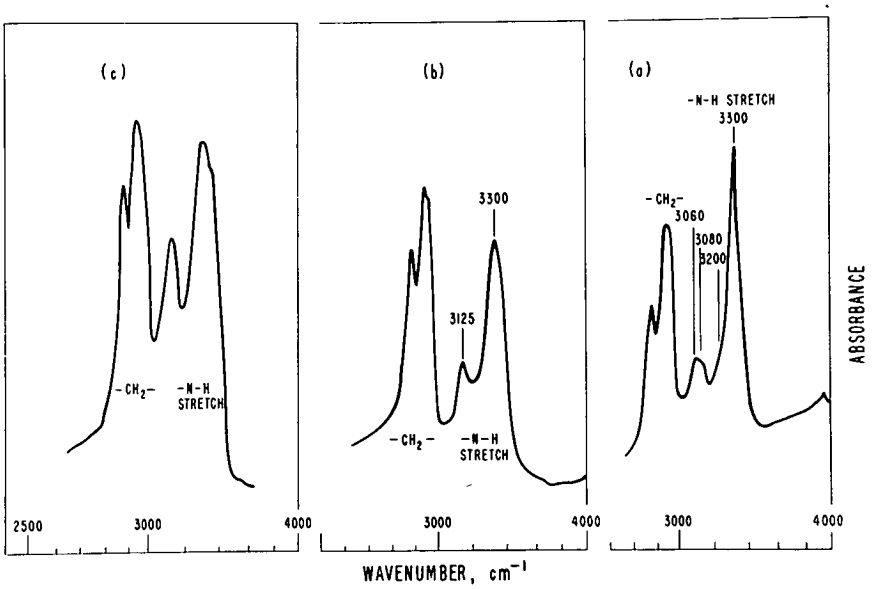

Fig. 2. Spectral changes in nylon 6 treated with Type I metal halides: N–H stretching band region. (*a*) untreated; (*b*) treated with $ZnCl_2$; (*c*) treated with $CuCl_2$.

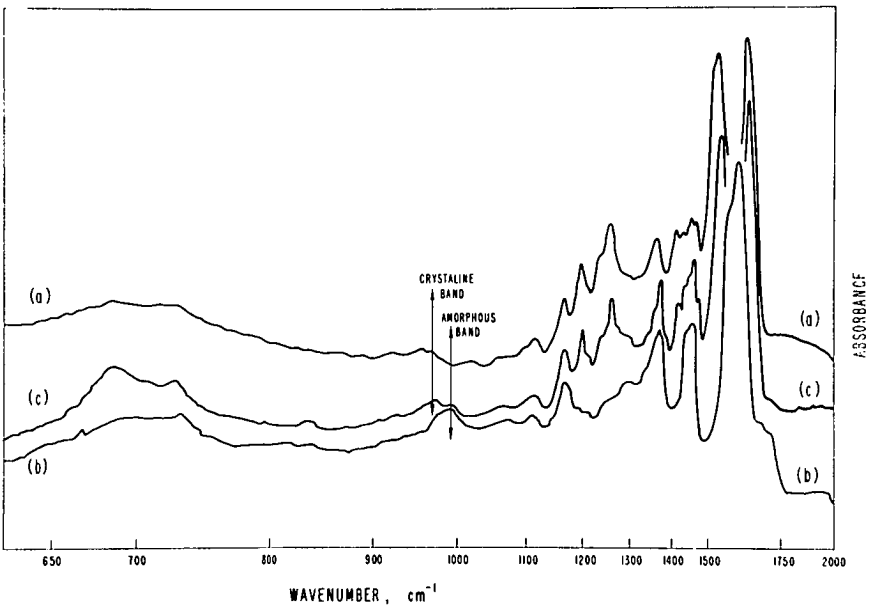

Fig. 3. Spectral changes in cast nylon 6 film containing $ZnCl_2$: spectral region 600-2000 cm^{-1}. (*a*) cast film, control; (*b*) cast film containing $ZnCl_2$; (*c*) cast film containing $ZnCl_2$ after leaching with water.

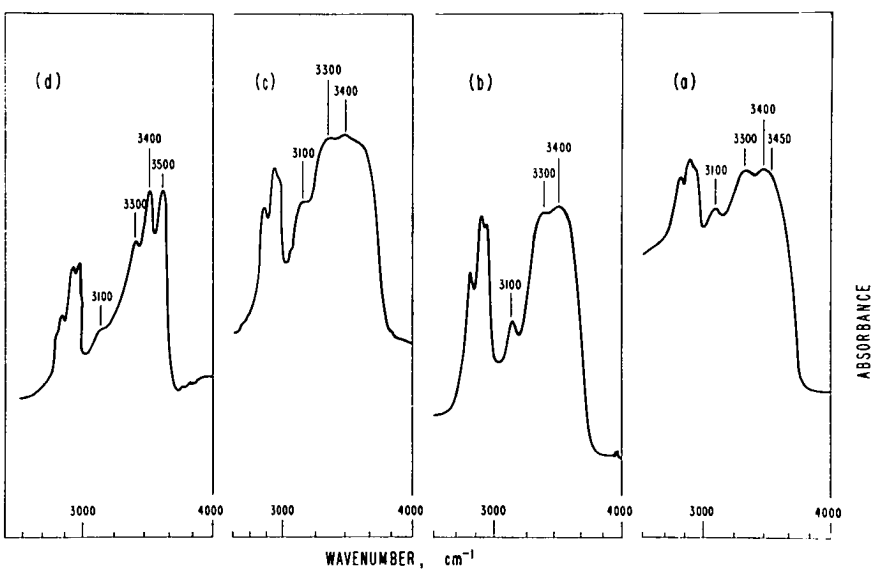

Fig. 4. Spectral changes in cast nylon 6 film containing Type II metal halides: N—H stretching band region. (*a*) With LiCl; (*b*) with $CaCl_2$; (*c*) with $MgCl_2$; (*d*) with $NiCl_2$. A spectrum of a nylon film control is shown in Figure 2*a*.

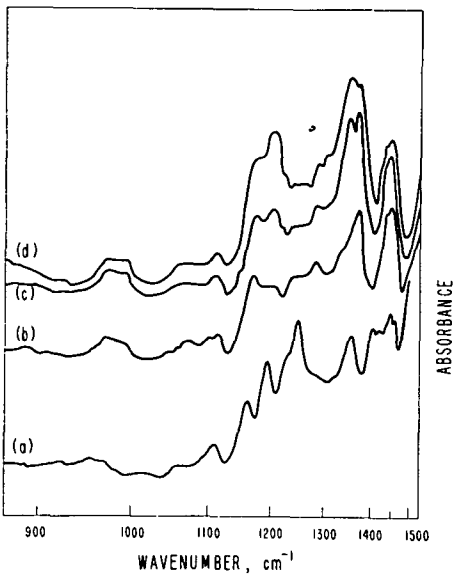

Fig. 5. Spectral changes in cast nylon 6 film containing Type II metal halides: spectral region 900-1500 cm^{-1}. (*a*) Untreated; (*b*) with LiCl; (*c*) with $CaCl_2$; (*d*) with $MgCl_2$.

without washing, showed distinctive changes in their infrared spectra. In the unwashed, but dried films, clarity was unimpaired but the films were swollen and elastic rather than tough. On washing and redrying these films, a change to the normal nylon 6 spectrum occurred and the films became opaque.

Films treated for various periods (15, 30, 60, 120, 240 min) with aqueous zinc chloride solution, showed cumulative changes in their spectra. These changes, as shown in Figure 1, were not due to excess zinc chloride solution at the surface as polypropylene films, treated in the same way, showed no changes in their infrared spectra. Some reagents such as methanolic $cobalt_{II}$ chloride required treatment at high temperatures to induce modifications to the nylon 6 spectra.

Cast films produced from mixed solutions of nylon 6 and metal halides in methanol/formic acid gave spectra of the same type as those associated with nylon films treated with solutions of the corresponding metal halides. Details of spectra, as given in Tables I and II, indicated that active metal halides could be divided into two types according to the modifications they induced in the spectra of nylon 6 films.

Type I: Zinc chloride, $cobalt_{II}$ chloride, $copper_{II}$ chloride, $iron_{III}$ chloride, $chromium_{III}$ chloride and $manganese_{II}$ chloride

Type II: Lithium chloride, lithium bromide, magnesium chloride and calcium chloride

Cast nylon 6 films containing Type I metal halides all gave spectra with a characteristic new absorption band at about 1595 cm^{-1} which was not

TABLE I
Infrared Data on Nylon 6 Films Treated with Metal Halides

Treatment, time	3080 3060 cm^{-1} band		Spectral data, cm^{-1}				Position of new band
			Amide I band		Amide II band		
	Position,	Shift	Position,	Shift	Position,	Shift	
Nylon 6 film							
untreated	3060	Nil	1637	Nil	1530	Nil	—
Aqueous $ZnCl_2$							
15 min	3080	+20	1625	−11	1537	+7	1595
30 min	3090	+30	1630	−7	1537	+7	1595
60 min	3090	+30	1630	−7	1537	+5	1595
120 min	3110	+50	1630	−7	1540	+10	1595
240 min	3120	+60	1625	−11	1555	+25	1595
Aqueous $CoCl_2$							
1 week	3120	+60	1637	Nil	1540	+10	Nil
Methanolic $CoCl_2$							
1 min at the boiling point	3080	+20	1630	−7	1540	+10	1595
HCl solutions							
1.7N, 60 min	3060	Nil	1635	−2	1535	+5	Nil
2.2N, 60 min	3060	Nil	1630	−7	1530	Nil	Nil
2.2N, 120 min	3060	Nil	1635	−2	1530	Nil	Nil
2.2N, 180 min	3060	Nil	1635	−2	1530	Nil	Nil
4.5N, 60 min	3060	Nil	1630	−7	1530	Nil	Nil
Cast films							
Nylon 6/$ZnCl_2$	3125	+65	1605(?)	−32	1580	+50	1595
Nylon 6/$CoCl_2$	3140	+80	1610(?)	−27	1580(?)	+50	1595
Nylon 6/HCl	3060	Nil	1635	−2	1530	Nil	Nil

present in nylon films containing Type II metal halides. Type II halides caused the formation of a broad band in treated nylon films at about 3400^{-1}, but Type I halides did not. Films treated with nickel$_{II}$ chloride showed spectral changes similar to those caused by both Type I and Type II halides. The new absorption band at 1595 cm^{-1} in the spectra of nylon 6 containing Type I metal halides increased in intensity with increasing time or temperature of treatment. Simultaneously the amide I and amide II bands, at 1637 cm^{-1} and 1530 cm^{-1} respectively, decreased in intensity and showed shifts towards each other until both bands were hidden in the new band. Major changes also occurred in the N—H stretching band at about 3300 cm^{-1} which became broadened and showed reduction of the height of the band. Marked shifts also occurred in the small bands at 3060 cm^{-1} and 3080 cm^{-1} in nylon 6. These changes are shown for nylon 6 films treated with zinc chloride, in Figures 1 and 2.

Other changes were also observed in the spectra of nylon 6 films treated with Type I metal halides. Two bands, at 1460 and 1480 cm^{-1}, appeared in films treated with aqueous zinc chloride, and replaced the four C—H

TABLE II
Infrared Data on Cast Nylon 6 Films Treated with Metal Halides

Cast films	Spectral data, cm^{-1}								
	N—H stretch		3080–3060 cm^{-1} Band		Amide I band		Amide II band		Position of new band
	Position,	Shift	Position,	Shift	Position,	Shift	Position,	Shift	
Untreated nylon 6	3300	—	3080/3060	—	1637	—	1530	—	—
Nylon 6/HCl	3300	Nil	3060	—	1635	−2	1530	Nil	Nil
Type I Halides									
Nylon 6/$ZnCl_2$	3300	Nil	3135	+75	1605(?)	−32	1580	+50	1595
Nylon 6/Zn(OAc)2	3360(?)	+60	3060	Nil	1637	Nil	1530	Nil	Nil
Nylon 6/$CoCl_2$	3300	Nil	3140	+80	1610(?)	−27	1580(?)	+50	1595
Nylon 6/$CoSO_4$	3300	Nil	3060	Nil	1637	Nil	1530	Nil	Nil
Nylon 6/$CrCl_3$	3300	Nil	3130	+70	1625	−12	—	—	1595
Nylon 6/$NiCl_2$	3300	Nil	—	—	1635	− 2	1575	+45	1595, 3400, 3500
Nylon 6/$CuCl_2$	3300	Nil	3120	+60	1635	− 2	1560	+30	1595
Nylon 6/$FeCl_3$	3300	Nil	—	—	1595	−42	1530	Nil	1595
Nylon 6/$MnCl_2$	—	—	—	—	—	—	—	—	1595
Type II Halides									
Nylon 6/LiCl	3250	−50	3100	+40	1635	− 2	1550	+10	3400, broad
Nylon 6/$MgCl_2$	—	—	—	—	1635	− 2	1560	+30	3400, broad
Nylon 6/$CaCl_2$	3300	Nil	3100	+40	1625	−12	1562	+32	3450, broad
Nylon 6/CdI_2[a]	—	—	—	—	1630	− 7	1545	+15	1595, shoulder

[a] Solubility limitations prevented the addition of excess CdI_2.

deformation bands at 1500, 1480, 1460 and 1420 cm^{-1} in normal nylon 6 spectra. The sharp band at 1200 cm^{-1} was eliminated and the band in the amide III region replaced by a broad absorption band at 1275 cm^{-1}. These spectral changes in the region 2000–650 cm^{-1}, for nylon 6 films treated with zinc chloride, are shown in Figure 3.

Treatment of nylon 6 films with Type II metal halides gave smaller shifts in the amide I and amide II bands similar to those for Type I reagents, as shown in Table II, without the appearance of a new band at 1595 cm^{-1}. Marked spectral changes occurred in the N—H stretching region in cast films containing nickel, magnesium, calcium or lithium chloride and these are shown in Figure 4. Other changes in the 1550–900 cm^{-1} region with cast films include appearance of double absorbance at about 1460 and 1480 cm^{-1}, doubling of the band at about 1350 cm^{-1} and partial or complete elimination of the bands at 1200 cm^{-1} and 1250 cm^{-1}. These spectral changes in cast films containing lithium chloride, calcium chloride and magnesium chloride are shown in Figure 5.

Nylon 6 films treated with dilute hydrochloric acid show only very minor changes in spectra, as shown in Tables I and II.

Action of Metal Halides on Model Compounds

In order to interpret the spectral changes observed in treated nylon 6 films, the action of metal halides on secondary amide model compounds was investigated. These compounds were, *N*-ethyl acetamide, ϵ-caprolactam and *N*-methyl-2-pyrrolidone.

Spectral data for solutions of zinc chloride and hydrogen chloride in *N*-ethyl acetamide and for complexes of *N*-ethyl acetamide with zinc chloride and cobalt chloride are given in Table III. The spectra of the complexes show large shifts in the amide I and amide II bands and the appearance of a new band at 1595 cm^{-1}.

ϵ-Caprolactam and $cobalt_{II}$ chloride gave products of different melting points depending on the mole ratio of reactants used. The products were:

Mole ratio, caprolactam: $CoCl_2$, 12:1, mp., 68°C; 6:1, mp., 87–90°C; 2:1, mp., 100–103°C; 1:1, mp., 113–115°C

The products were all blue crystalline solids and they showed progressive changes from the normal spectrum of ϵ-caprolactam. The changes included a shift of the 1655 cm^{-1} band to 1525 cm^{-1} and the appearance of a new absorption band at 1595 cm^{-1}. The observed shift of -30 cm^{-1} in the amide I band and the appearance of the new absorption band at 1595 cm^{-1} were similar to the changes induced by $cobalt_{II}$ chloride in both nylon 6 films and *N*-ethyl acetamide.

N-methyl-2-pyrrolidone formed a solid blue product of mp above 250°C, with $cobalt_{II}$ chloride. With zinc chloride a solid derivative could not be obtained but a viscous liquid product was formed. The infrared spectra of these $cobalt_{II}$ and zinc products showed distinctive changes from the

TABLE III
Infrared Data on Model Compounds Treated with Metal Halides

Sample	Spectral data, cm^{-1}								
	N—H stretch		3086 cm^{-1} Band		Amide I band		Amide II band		Position of new band
	Position,	Shift	Position,	Shift	Position,	Shift	Position,	Shift	
N-ethyl acetamide (NEA)	3290	—	3086	—	1640	—	1537	—	—
NEA/$ZnCl_2$[a] (dilute solution)	3300	+10	3080	− 6	1640	Nil	1537	Nil	1612
NEA/$ZnCl_2$[a] (concentrated solution)	3300	+10	3090	+ 4	1630	−10	1545	+ 8	1600
NEA/$ZnCl_2$[a] complex	3330	+40	3140	+54	1612	−28	1570	+33	1595
$NEA_2/CoCl_2$[a] complex[b]	3330	+40	3130	+44	1620	−20	1565	+28	1595
NEA saturated with dry HCl	3250	−40	3060	−20	1640	Nil	1550	+13	Nil

[a] These results are similar to those reported for the effect of $ZnCl_2$ and $CoCl_2$ on nylon 6 films (Table II).
[b] Solid blue-green complex, mp. 15°C.

spectrum of *N*-methyl-2-pyrrolidone. Of these, the most important were the shifts of the carbonyl absorption band at 1665 cm^{-1} to lower frequencies. Measured shifts for zinc chloride and $cobalt_{II}$ chloride derivatives were -35 cm^{-1} and -65 cm^{-1} respectively.

Because of solvent difficulties it was not possible to carry out high resolution NMR studies on nylon 6 in the presence of metal halides. Studies were carried out on the model compound *N*-ethyl acetamide and its metal halide derivatives.

The $cobalt_{II}$ chloride complex of *N*-ethyl acetamide was also unsuited to NMR investigation because of the gross line broadening due to the highly paramagnetic cobalt. However with *N*-ethyl acetamide and zinc chloride (mole ratio 2:1), in acetone, the difference in chemical shift between the complex and pure *N*-ethyl acetamide was +25 cps for $[CO+CH_3$ and +13 cps for $[N+CH_2$.

DISCUSSION

Coordination of Nylon by Type I Metal Halides

The agreement between the spectra of nylon 6 treated with Type I metal halides and the spectra of the model amide derivatives suggests the formation of a coordination complex, in which the polyamide or amide acts as the ligand. Examination of the spectra of the reaction products of Type I metal halides and primary and secondary, aliphatic, aromatic and heterocyclic amines and diamines showed spectra modifications which showed the formation of a nitrogen atom-metal ion coordinate bond. Our observations agreed with those of Graddon, Heng and Watton[2] and Gill and Kingdon.[3] The absence of similar spectral characteristics in the spectra of treated nylon 6 films and amide derivatives indicated that a coordinate bond between the metal ion and the amide group nitrogen atom was unlikely.

The strong shifts observed in the amide I and amide II bands of treated nylons and amide derivatives, however, suggest that the structure of the amide group has been modified. Bull, Madan and Willis[4] have described oxygen-metal bonded complexes between *N*,*N*-dimethyl acetamide and metal halides, and have shown that marked shifts of the amide I band to lower frequencies occur. The similar shifts observed in treated nylon 6 films and amide derivatives indicate that an oxygen-metal bond is present. Carty[5] has also described the NMR and infrared spectra of some zinc halide complexes of N,N-dimethyl acetamide (DMA). Shifts of the amide I band to lower frequencies and of the amide II band to higher frequencies were observed together with the appearance of new bands at 1618 cm^{-1}, 1622 cm^{-1} and 1610 cm^{-1} for the DMA complexes with zinc chloride, bromide and iodide respectively. Typical shifts for complexes with zinc chloride are shown in Table IV.

TABLE IV
Band Shift for Amide—Zinc Chloride Complexes

	Band Shift, cm^{-1}			
	DMA[4]	DMA[5]	*N*-ethyl acetamide	Nylon 6
Amide I band shift	−42, −59	−60	−28	−32
Amide II band shift	—	+18	+33	+50
New band position, cm^{-1}	—	1618	1595	1595

Carty[5] and Kuhn and McIntyre[6] have described the NMR spectra of complexes of zinc chloride and *N,N*-dimethyl acetamide and *N,N*-dimethyl formamide respectively. Their reported chemical shifts are similar to the shifts observed for the zinc chloride-*N*-ethyl acetamide derivative in acetone solution, as shown in Table V. On this evidence, the amide

TABLE V
Chemical Shifts for Amide—Zinc Chloride Complexes

Compound	Chemical Shift, cps.			
	[CO]—CH_3	[CO]—H	[N]—CH_3	[N]—CH_2—
$HCONMe_2:ZnCl_2$ (2:1)[6]	—	+13.0	+14, +17[a]	—
$CH_3CONMe_2:ZnCl_2$(2:1)[5]	+18.6	—	+10.2	—
$CH_3CONHEt:ZnCl_2$(2:1)	+25.0	—	—	+13.0

[a] *Cis* and *trans* methyl groups distinguished.

group in nylon 6 treated with Type I metal halides appears to be linked to the metal ion through the oxygen atom.

Structure of Type I Metal Halide—Amide Complexes

According to Bellamy[7] the N—H stretching frequency of amides in *cis*-form is about 100 cm^{-1} lower than that of *trans*-form, and that an appreciably higher N—H deformation frequency would be expected. In the *cis*-form the amide II band would be expected to approach very close to the amide I band and may coincide with it. Cyclic lactams, such as caprolactam and 2-pyrrolidone, which are only present in the *cis*-form show only one band. The shifts of the amide I and amide II bands, together and the appearance of a new band at 1595 cm^{-1}, in nylon 6 treated with Type I metal halides, and in *N*-ethyl acetamide derivatives (Tables I and II) may be explained by a *trans*- to *cis*-transformation in addition to the shift of the carbonyl stretching frequency to a lower value due to the formation of a carbonyl-metal coordinate link.

Shifts to a higher frequency were noted for the absorption bands at 3086 cm^{-1} in *N*-ethyl acetamide and at 3060 and 3080 cm^{-1} in nylon 6 when treated with Type I metal halides, together with corresponding shifts in the amide II band. The observed shifts bring these bands to a fre-

quency very close to that observed in the spectrum of 2-pyrrolidone and other lactams in which the amide exists in the *cis*-form only and confirms that these bands are in fact overtones of the amide II band.

The broadening and reduction in band height of the N—H stretching frequency in nylon 6 films treated with Type I metal halides is typical and can be seen in Figure 2 for nylon 6 films treated with copper$_{II}$ chloride and zinc chloride. Higher resolution spectra are shown in Figure 6.

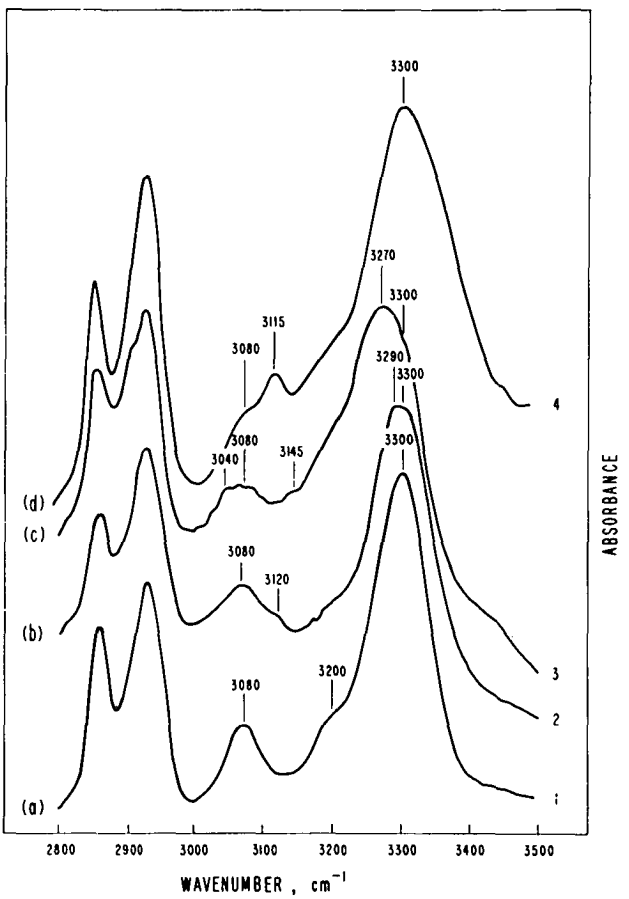

Fig. 6. Spectral changes in nylon 6 film treated with aqueous $ZnCl_2$ (80%): N—H stretching band region—high resolution spectra. (*a*), untreated; (*b*), treated, 50 min.; (*c*), treated 120 min.; (*d*), treated, 10 min. at 100°C.

We believe that the N—H stretching band in nylon 6 at about 3300 cm^{-1} is a composite band consisting of a higher frequency *trans*-form contribution and a lower frequency *cis*-form contribution. The nonsymmetry of the band with a low frequency shoulder and the subsequent changes on treatment with metal halides can be explained by increasing change of structure from the *trans*- to the *cis*-form. On this basis we have proposed

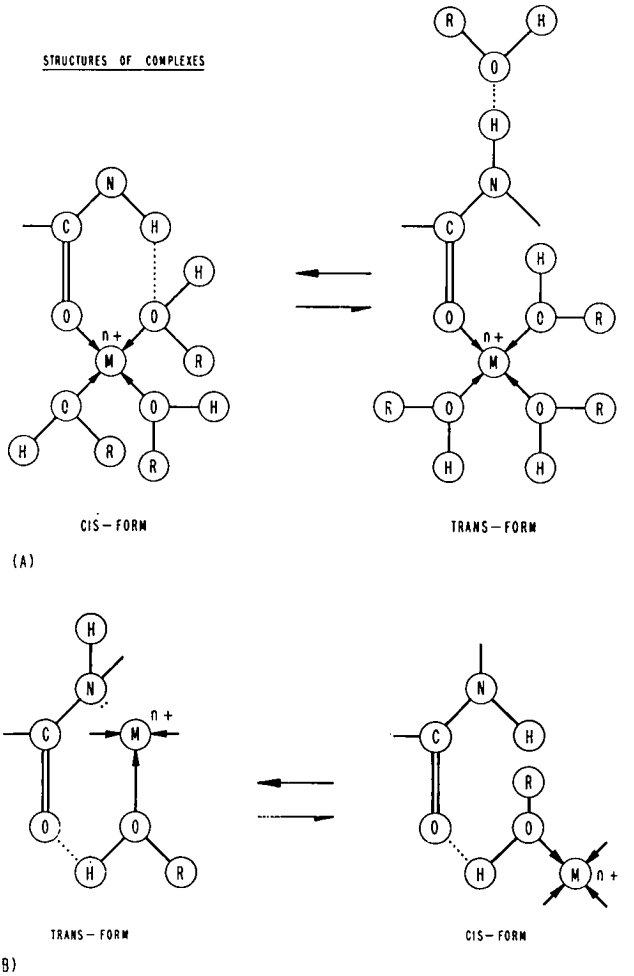

Fig. 7. Proposed structures for complexes with polyamides: *a*, with Type I metal halides; *b*, with Type II metal halides.

a cyclic *cis*-form complex, as shown in Figure 7*a*, for nylon 6 and amide products with Type I metal halides.

The Amorphous Nature of Nylon 6 Treated with Metal Halides

The changes observed in the spectra of nylon 6 treated with metal halides, of both Types I and II, in the region 1500-650 cm^{-1} have been described and are shown in Figures 3 and 5. The changes are such that spectral features similar to those in the spectra of amorphous, steric hindered 1,1-dimethyl substituted nylon 66 as reported by Cannon[8] are visible. This result is ascribed to a change in the nylon from the crystalline form to a more amorphous form, when it is complexed with the metal halide.

The Action of Type II Metal Halides

In Part I,[1] calcium, lithium and magnesium chlorides were shown to be inactive as stress cracking agents in aqueous solution but active in methanolic solution. Nylon films treated with these agents gave different spectral changes as compared to films treated with Type I metal halides and a different action is proposed. The absence of the new band at 1595 cm^{-1} and only minor shifts in the amide I and amide II bands (see Tables I and II) indicate that coordination between the oxygen of the amide group and the metal ion is unlikely.

The broad absorbance above 3300 cm^{-1} noted in nylon 6 films treated with Type II metal halides is similar to the observations reported by Sarda and Peacock[9] for nylon 6 and 66 films treated with lithium or magnesium perchlorates or lithium bromide. Spectral details are shown in Figure 4.

In the spectrum of nylon 6 film, the N—H stretching frequency at about 3300 cm^{-1} is about 100 cm^{-1} lower than the normal free N—H stretching frequency of amides in dilute solution. According to Rao[10] this could indicate the presence of hydrogen bonding. The new broad absorbances observed in films treated with Type II metal halides (LiCl, LiBr, $CaCl_2$ $MgCl_2$ etc.) can then be interpreted as free N—H stretching absorptions resulting from elimination of hydrogen bonding.

Methanolic solutions of Type II metal halides act as proton donating agents in a manner similar to phenol and formic acid. These preferentially hydrogen bond with the amide carbonyl oxygen and cause solution of the nylon. The proposed structure of the Type II metal halide-nylon 6 product is shown in Figure 7*b*.

We believe the different behaviour of the Type II metal halides in various solvents, especially in water and in methanol, is dependent on the degree of solvation of the halide. For hydrogen bonding between the reagent and the carbonyl oxygen atom to occur, the charge distribution over the protons of the solvated metal salt must be highly localised. For example, calcium chloride in aqueous solution is hydrated with at least 6 molecules of water in the coordination sphere of the calcium ion, and the charge density on each proton is $+2e/12$. However calcium chloride in methanolic solution exists as the alcoholate, $CaCl_2.(CH_3OH)_4$[11] and in this case the charge density on each proton is much greater, $+2e/4$, making it a stronger proton donor.

Nickel$_{II}$ chloride represents a singular case, presenting features of both Type I and Type II metal halides. Like Type I agents, with nylon 6, it gives large shifts of the amide I and amide II bands and a new absorption band at about 1595 cm^{-1}. Like Type II agents it gives absorption bands above 3300 cm^{-1} in which two distinct bands at 3400 and 3500 cm^{-1} are observed. Details are given in Table II and Figure 4.

The absorption bands at 3400 and 3500 cm^{-1} respectively are believed to be due to two free N—H stretching frequencies. The lower frequency

band resulting from a normal free N—H absorption and the higher frequency band from an acidic proton N—H stretching absorption. The acidic proton is believed to result from some delocalization of the lone pair of electrons on the nitrogen atom as a result of the proximity of the metal ion in the cyclic structure proposed (Fig. 7*b*).

Mechanism of Stress-cracking

The stress-cracking of nylon 6 by metal halides appears to be due to two distinct mechanisms.

With Type I metal halides, physical effects such as surface wetting and localised notch stresses may contribute to crack initiation. However, the major effects are migration of the metal halide into the nylon where it is attracted to the dipolar amide groups. As a result, hydrogen bonding between polymer chains is weakened, and the amide N—H protons form bonds with the conditioning agent (normally water) or with hydrated metal halide molecules. This effectively sheathes the nylon chains with solvent molecules and causes local plasticisation and swelling of the nylon, increasing the internal stresses. Also formation of a complex between the amide group of the nylon and the solvated metal halide occurs, and this destroys interchain hydrogen bonding, replacing it with intra-chain hydrogen bonding as shown in Figure 7*a*.

The complexed nylon with changed structure becomes more amorphous and as a result increased absorption of water or solvent can occur. This increases plasticization, lowers the yield stress of the nylon and rupture occurs.

The complex between nylon and Type I metal halides is rapidly destroyed by excess water or other oxygen containing solvents. This accounts for the "reversion" of the spectrum of treated nylon 6 films, on washing.

Higher temperatures promote cracking by allowing more rapid migration of the metal halide to occur. As the level of conditioning agent in the nylon is increased the initial yield stress is reduced and a more effective pathway for migration of the metal halide into the nylon is provided. In dry nylon migration cannot occur.

Type II metal halides are essentially true solvent cracking agents in that solution of the nylon by the proton donating system occurs, as with phenol and formic acid, and this results in rupture of stressed specimens.

The action of metal thiocyanates on nylon 6 films has been studied and the results confirm our proposed mechanism. These studies are described in Part III.

References

1. P. Dunn and G. F. Sansom, *J. Appl. Polymer Sci.*, **13**, No. 8 (1969).
2. D. P. Graddon, K. B. Heng, and E. C. Watton, *Aust. J. Chem.*, **19**, 1801 (1966).
3. N. S. Gill and H. J. Kingdon, *Aust. J. Chem.*, **19**, 2197 (1966).
4. W. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 303 (1963).
5. A. J. Carty, *Can. J. Chem.*, **44**, 1881 (1966).

6. S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 375 (1965).
7. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methven and Co. Ltd., 1958, p. 217, London.
8. G. C. Cannon, *Spectrochim Acta*, **16**, 302 (1960).
9. G. Sarda and N. Peacock, *Nature*, **200**, 67 (1963).
10. C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, 1963, London.
11. E. H. Rodd, *Chemistry of Carbon Compounds*, Volume 1A, Elsevier, 1951, p. 298, London.

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The Stress Cracking of Polyamides by Metal Salts. Part III. Metal Thiocyanates

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Synopsis

The stress cracking of polyamide (nylon 6) by a number of metal thiocyanates in aqueous and nonaqueous solutions has been investigated. Lithium, zinc and cobalt$_{II}$ thiocyanates were the most active and their activity was compared with that of the corresponding metal halides. Stress cracking parameters were determined and the mechanism of cracking studied by infrared techniques. The action of metal thiocyanates on nylon 6 is similar to that of the corresponding metal halides. Some metal cobaltothiocyanates were also found to be active stress cracking agents.

INTRODUCTION

The action of metal halides on polyamides (nylons) has previously been reported.[1–6] In our early work, Parts I[2] and II,[3] we have described the action and mechanism, respectively of metal halides and certain other salts on polyamides.

On the basis of the observed stress rupture of polyamides by metal halides it was predicted that halide-like salts, especially the thiocyanates, should be effective stress cracking agents for nylons. In initial screening trials, it was noted that in concentrated aqueous solution, ammonium thiocyanate, barium thiocyanate, calcium thiocyanate, zinc thiocyanate, lithium thiocyanate, cobalt$_{II}$ thiocyanate and ferric thiocyanate, all caused rupture of thin, stressed nylon films. This paper describes the stress cracking activity and behavior of metal thiocyanates on nylons.

EXPERIMENTAL

Nylon 6 (Trogamid B) extruded sheet, as described in Part I,[2] and 0.001 in. thick extruded, blown, unplasticized, nylon 6 film, as described in Part II,[3] were used as specimens for the determination of stress cracking parameters. Lithium, barium, zinc, cobalt$_{II}$, ammonium and potassium thiocyanates were laboratory reagent grades, and were used, without further purification, in aqueous and methanolic solutions.

Calcium thiocyanate was obtained as a 50% w/w solution, and was used in this form for studies of activity in aqueous solution. Methanolic

solutions were prepared by evaporating a known amount of aqueous solution to dryness, under vacuum, and then adding the required amount of methanol.

Ferric thiocyanate was prepared by the addition of a saturated aqueous solution of ferric chloride to a saturated solution of ammonium thiocyanate in the stoichiometric ratio required. The aqueous solution containing the ferric thiocyanate was then extracted with diethyl ether and the ether extracts washed with distilled water. The ether extracts were then evaporated to dryness and the ferric thiocyanate recovered.

The cobaltothiocyanates used in the work were prepared by addition of a saturated aqueous solution of the corresponding metal thiocyanate to a saturated aqueous solution of cobalt$_{II}$ chloride in the stoichiometric ratio required. The cobaltothiocyanates precipitated on standing and were filtered and recrystallized twice from distilled water. The ammonium, potassium, calcium, barium, zinc and mercuric cobaltothiocyanates were prepared in this manner.

Insoluble mercuric cobaltothiocyanate was prepared as a check on the method of preparation of the other cobaltothiocyanates. The physical properties of the prepared compounds agreed with reported data.

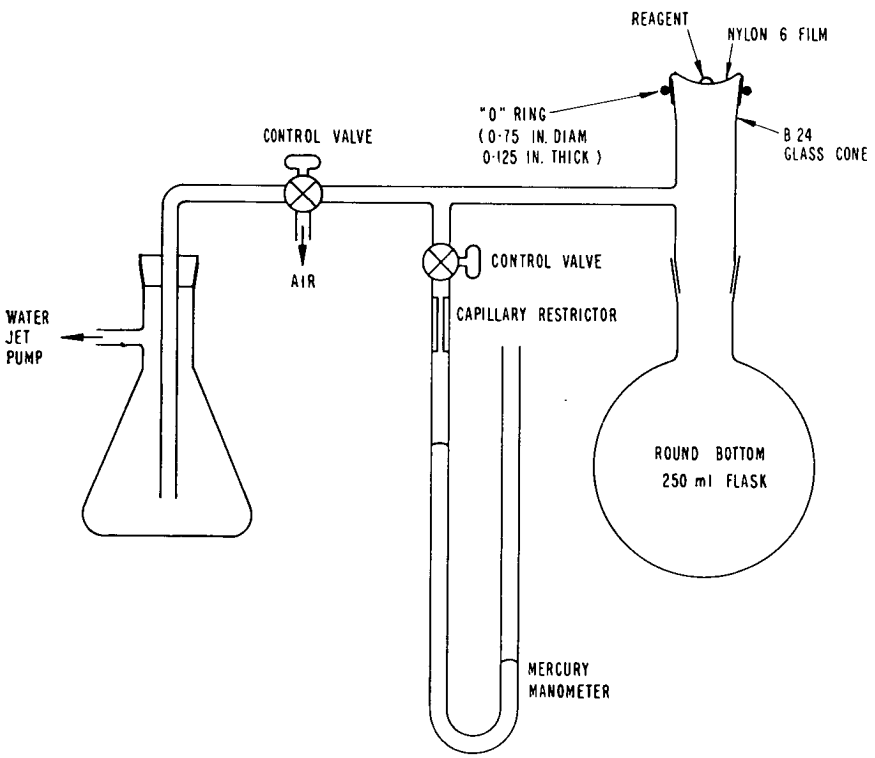


Fig. 1. Schematic diagram of apparatus used in the study of stressed nylon films (not to uniform scale).

TECHNIQUES

Nylon films and tensile bar specimens were used to obtain infrared data and stress cracking parameters by the technique described in Parts I[2] and II[3]. All infrared spectra were obtained using a Beckman IR8 or a Perkin-Elmer 125 recording spectrometer.

A new technique using stressed nylon 6 film was used to determine stress cracking parameters of metal thiocyanates. Nylon 6 film, 0.001 in. thick, was supported over a glass annulus by a rubber "O" ring, as shown in Figure 1, and stressed by the application of a reduced pressure on one side of the film. The pressure differential was indicated by a mercury manometer and from this the stress at the centre of the film could be calculated. A single drop of stress cracking reagent was applied at the central surface of the stressed film, and time to failure measured with a stopwatch. Film rupture at failure was indicated by a sudden loss of pressure as recorded by the manometer.

This technique enabled very rapid screening of compounds to be carried out and also gave information on the cracking activity of dilute solutions which could not be obtained using bulkier specimens.

RESULTS

Stressed Film Results

In nylon 6 films stressed by the technique described above, the actual tensile stress at the center of the film was calculated using the relationship reported by Roark,[7]

$$S = 0.423 \left[\frac{Ew^2a^2}{t^2} \right]^{1/3}$$

where

S = tensile stress at the centre of the film, psi

w = instantaneous loading = $P \times \frac{14.96}{32.05}$ (P = pressure in inches of Hg)

a = radius of annulus = 0.5 in.

t = thickness of nylon 6 film = 0.001 in.

E = Young's modulus of nylon 6 film. A 1000 second value for this time dependent property of 1×10^5 psi for nylon 6, at 23°C, and water content of 4.75%, was used.

Substituting these values, the relationship between tensile stress (S) and differential pressure (P) becomes;

$$S = 744.3\ P^{2/3}$$

This relationship is shown graphically in Figure 2 over the working range of pressures. Nylon 6 films stressed in this way yielded over the differential pressure range, 18.5–19.0 in. of mercury. From Figure 2, the

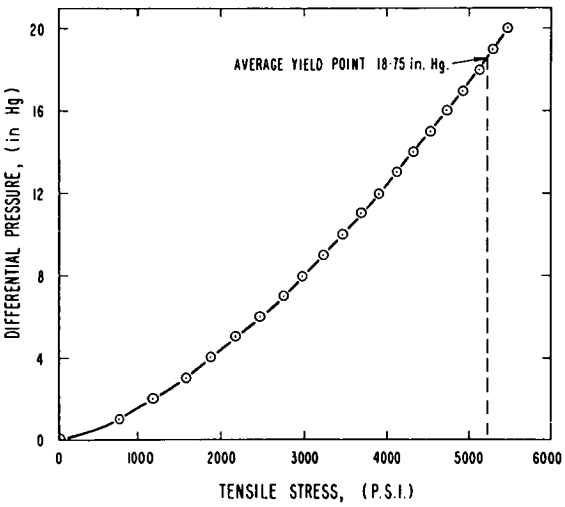


Fig. 2. The relationship between differential pressure and calculated stress at the center of stressed nylon 6 film.

average tensile yield stress from the above relationship, is 5250 psi. The tensile yield stress of the film, determined using a tensometer was found to be 5310 psi for specimens cut parallel to the direction of extrusion of the film and 5520 psi for specimens cut at right angles.

The lower value correlates well with the tensile yield stress calculated from the differential pressure, at yield, of the supported film.

The activity of aqueous solutions of metal thiocyanates and some halides was investigated using the stressed film technique. A measure of the activity of 1 *M* solutions is the critical stress (Sc) at which, or below which, stress rupture is slow and times to failure are greater than 300 sec. The critical stress for 1 *M* solutions of metal salts are given in Table I.

TABLE I
Activity of Aqueous Solutions on Stressed Nylon 6 Films

Solution in water (1 molar)	Concentration, % (w/v)	Critical pressure differential, in. of Hg	Approximate critical stress, psi
$Zn(SCN)_2$	18.16	2–3	1360
$Co(SCN)_2 \cdot 3H_2O$	22.92	2–3	1360
HCl	3.65	12–13	4000
$ZnCl_2$	13.63	12–13	4000
$Ca(SCN)_2 \cdot 3H_2O$	21.03	13–14	4220
$Ba(SCN)_2 \cdot 2H_2O$	28.96	13–14	4220
NH_4SCN	7.61	14–15	4420
LiSCN	6.50	16	4720
$Fe(SCN)_3$	23.01	16–17	4820
KCl	9.72	16–17	4820
NH_4SCN (2 molar)	15.22	16–17	4820

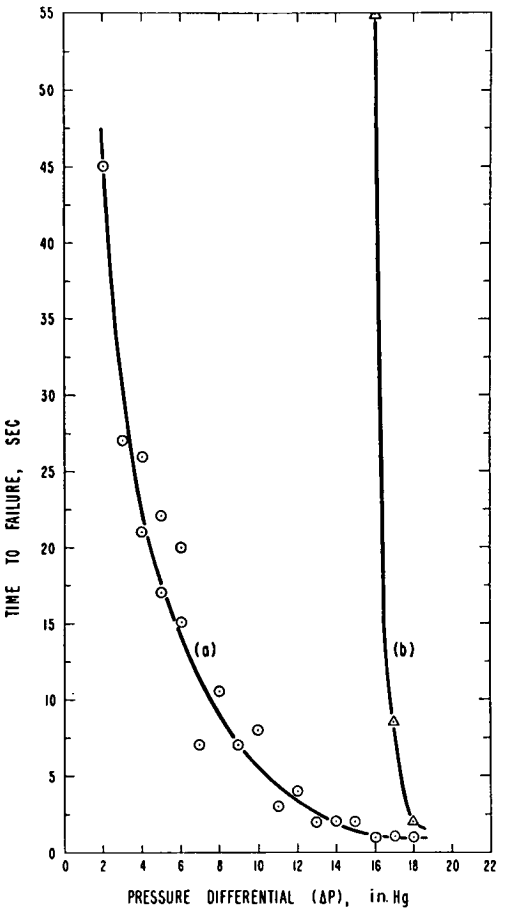


Fig. 3. The effect of stress on the time to failure of stressed nylon 6 films in contact with 1 *M* aqueous solutions of, (*a*), $Zn(SCN)_2$ and (*b*), $ZnCl_2$.

Using this technique, with dilute solutions it was shown that the activity of 1 *M* HCl and 1 *M* $ZnCl_2$ solutions were similar, and that even 1 *M* KCl would bring about rupture of films under high stress. This may appear to be in direct contrast to the results obtained with bulkier specimens and more concentrated solutions as described in Part I of this paper. However in dealing with more dilute solutions where extensive dissociation into ions has occurred, the rupture mechanism is believed to be one of simple ionic interference with hydrogen bonding between adjacent polymer chains and, as demonstrated, most salts are equally active at low concentrations. The stress dependence of time to failure for stressed films in contact with some 1 *M* solutions is shown in Figures 3 and 4.

With this technique film rupture was very rapid with concentrated solutions of metal salts, and generally dilute solutions were employed. The activity of zinc chloride solutions (25 and 50% w/v in water) has been

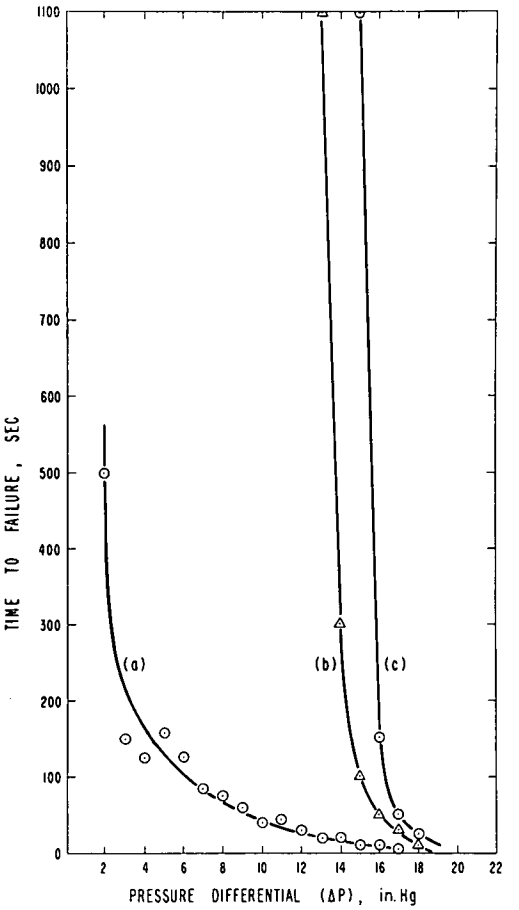


Fig. 4. The effect of stress on the time to failure of stressed nylon 6 film in contact with 1 *M* aqueous solutions of (*a*), $Co(SCN)_2$, (*b*), $Ca(SCN)_2$, and (*c*), Li SCN.

investigated using the stressed film technique and the results are shown in Figure 5.

Stress Cracking Parameters

The parameters, time to crack initiation, time to crack-through, time to rupture and the crack propagation rate were determined for solutions of thiocyanates in contact with stressed nylon 6 tensile bar specimens cut from extruded nylon 6 sheet using the techniques described in Part I.[2] Results are given in Tables II and III. The effect of stress on the time to crack-through and time to crack initiation of stressed nylon 6 tensile bar specimens in contact with aqueous zinc thiocyanate is shown in Figure 6. As indicated in Part I of this paper the crack propagation rates are a useful semi-quantitative measure of the activity of the cracking agents.

TABLE II
Stress Cracking Parameters for Metal Thiocyanates on Nylon 6 Tensile Bar Specimens

Compound	Concentration in aqueous solution, % (w/v)	Stressed at 2000 psi			Stressed at 4000 psi		
		Time to crack initiation (ΔT), min	Time to crack through (T_I), min	Time to rupture (T_R), min	Time to crack initiation (ΔT), min	Time to crack through (T_I), min	Time to rupture (T_R), min
$Zn(SCN)_2$	30	1.0	8.0	15	0.3	3.4	12
	36 (saturated)	0.1	3.7	10	0.1	2.2	7
$Ba(SCN)_2$	30	18	>1500	No rupture	20	>1500	No rupture
	92	0.7	50	230	0.02	0.7	10
	170 (saturated)	0.05	0.8	16	0.05	0.6	6
NH_4SCN	30	265	>1500	No rupture	6	>1000	No rupture
	160 (saturated)	120	>1000	No rupture	90	365	800 (approx)
LiSCN	30	>2000	>2000	>2000	>300	>1200	>1200
	saturated	0.15	0.3	1	0.15	0.25	1
$Co(SCN)_2$	30	>360	>360	360	0.4	30	82
	saturated	60	90	130	0.2	1	7
$Fe(SCN)_3$	30	76	87	170	36	100	180
	saturated	60	90	220 (approx)	0.4	80	185
$Ca(SCN)_2$	50	No crack initiation within 1500 min					
	100	No crack initiation within 1500 min					

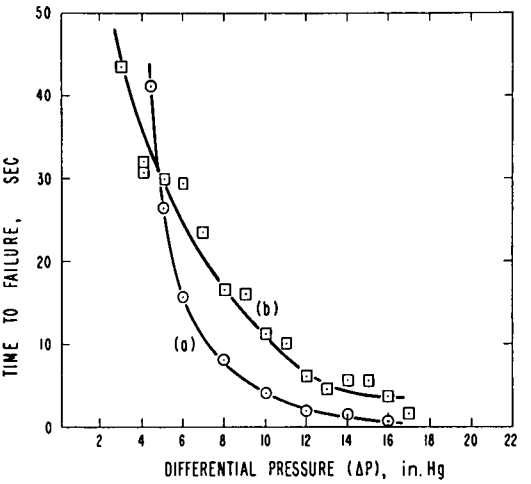


Fig. 5. The effect of stress on the time to failure of stressed nylon 6 films in contact with aqueous $ZnCl_2$, (*a*), 25% w/v and (*b*), 50% w/v.

Whilst numerical values are employed emphasis should only be placed on the order of magnitude.

Stress cracking data for metal thiocyanates indicates that in general these are more active than the corresponding metal halides. Crack prop-

TABLE III
Crack Propagation Rates (K) for Nylon 6 Stress-Cracked by Thiocyanate Solutions[a]

Solvent	Salt	Concentration	Crack propagation rate (K), in./min	
			2000 psi stress	4000 psi stress
Water	$Zn(SCN)_2$	30%	6.4×10^{-3}	1.5×10^{-2}
Water	$Zn(SCN)_2$	36% (satd)	1.2×10^{-2}	2.0×10^{-2}
Water	$Ba(SCN)_2$	30%	$<3.0 \times 10^{-5}$	$<3.0 \times 10^{-5}$
Water	$Ba(SCN)_2$	92%	9.0×10^{-4}	6.2×10^{-2}
Water	$Ba(SCN)_2$	170% (satd)	5.6×10^{-2}	7.0×10^{-2}
Water	$NH_4(SCN)$	30%	$<3.0 \times 10^{-5}$	$<3.0 \times 10^{-5}$
Water	$NH_4(SCN)$	satd	$<4.0 \times 10^{-5}$	1.2×10^{-4}
Water	$Fe(SCN)_3$	30%	5.0×10^{-4}	4.5×10^{-4}
Water	$Fe(SCN)_3$	satd	5.0×10^{-4}	5.6×10^{-4}
Water	Li(SCN)	30%	[b]	[b]
Water	Li(SCN)	satd	2.4×10^{-1}	4.8×10^{-1}
Water	$Co(SCN)_2$	30%	[b]	1.3×10^{-3}
Water	$Co(SCN)_2$	satd	1.3×10^{-3}	5.0×10^{-2}
Water	$Ca(SCN)_2$	100%	[c]	[c]
Methanol	$Ca(SCN)_2$	satd	—	1.5×10^{-4}
Methanol	Li(SCN)	satd	—	0.5

[a] Conditions: Nylon 6 specimens, water content 3.5%, at 21°C.
[b] Very slow crack propagation.
[c] No crack initiation occurred.

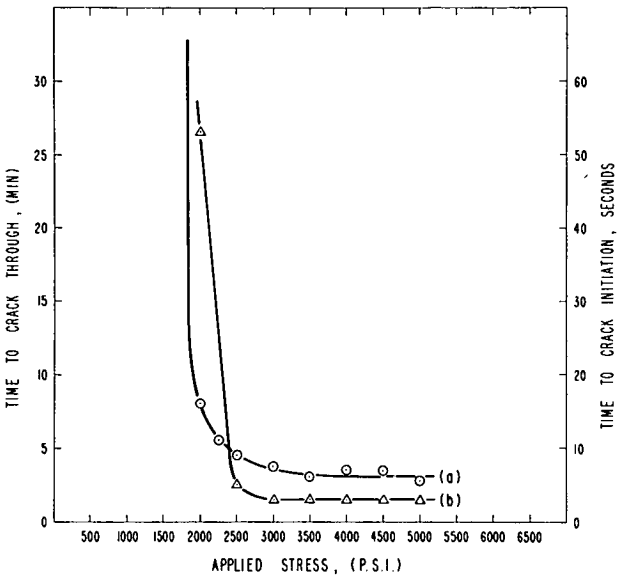


Fig. 6. The effect of stress on the time to crack-through, (*a*), and time to crack initiation (*b*), of stressed nylon 6 tensile bar specimens in contact with 30% w/v aqueous $Zn(SCN)_2$.

agation rate data (Table III) showed that saturated aqueous and methanolic solutions of lithium thiocyanate were extremely active stress cracking agents for nylon. The general activities of the thiocyanates and halides of some metals in both aqueous and methanolic solution are summarised in Table IV.

TABLE IV
Activity of Metal Halides and Thiocyanates

Solvent	Metal ion	Activity[a]			
		Thiocyanate	Chloride	Bromide	Iodide
Water	Zinc	+++	+++	+++	+++
Water	$Cobalt_{II}$	+++	++	++	0
Water	Calcium	−	−	0	0
Water	Barium	++	−	−	−
Water	Lithium	+++	+	+++	−
Water	$Iron_{III}$	++	+	0	0
Water	Ammonium	++	−	−	−
Methanol	Zinc	−	+++	+++	+++
Methanol	$Cobalt_{II}$	−	++	0	0
Methanol	Calcium	++	++	0	0
Methanol	Barium	−	−	++	++
Methanol	Lithium	+++	++	+++	++
Methanol	$Iron_{III}$	−	++	0	0
Methanol	Ammonium	−	−	−	−

[a] (+++) Highly active; (++) active; (+) weakly active; (−) inactive; (0) not tested.

The Action of Metal Thiocyanates on Nylon 6 Film

The action of metal thiocyanates on nylon 6 films was investigated by a study of the changes induced by the salts in the infrared spectrum of the polyamide.

Immersion of nylon 6 films in aqueous zinc thiocyanate solution for various periods of time produced progressive changes in the spectrum of the nylon, with the most obvious changes being in the amide I and amide II bands. These changes, shown in Figure 7, are similar to those produced by zinc chloride as reported in Part II.[3] The close association between absorption of the zinc thiocyanate and the observed shifts of the amide I and amide II bands, and the appearance of a new characteristic band at

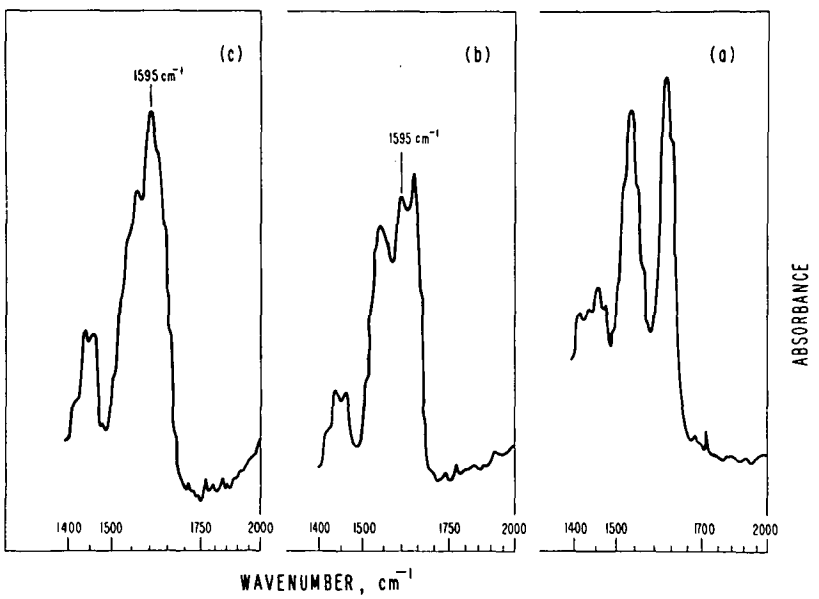


Fig. 7. Spectral changes in nylon 6 film treated with aqueous $Zn(SCN)_2$, (30% w/v): amide I and amide II band region. (*a*) untreated; (b) treated 20 min; (*c*) treated 60 min.

1595 cm^{-1}, is indicated by the simultaneous appearance of a strong —SCN band in the spectra. $Cobalt_{II}$ thiocyanate similarly caused shifts of the amide I and amide II bands, together with the appearance of a strong —SCN band. These are shown in Figure 8.

Other thiocyanates did not cause shifts in the amide I and amide II bands and gave weaker —SCN bands. With calcium thiocyanate, the —SCN band was extremely weak. The spectra of nylon 6 films treated with calcium and barium thiocyanates are shown in Figure 9. Lithium thiocyanate treated films rapidly became soft and rubbery and eventually dissolved completely in the reagent. The spectra of lithium thiocyanate treated films showed evidence of the film being highly amorphous in a

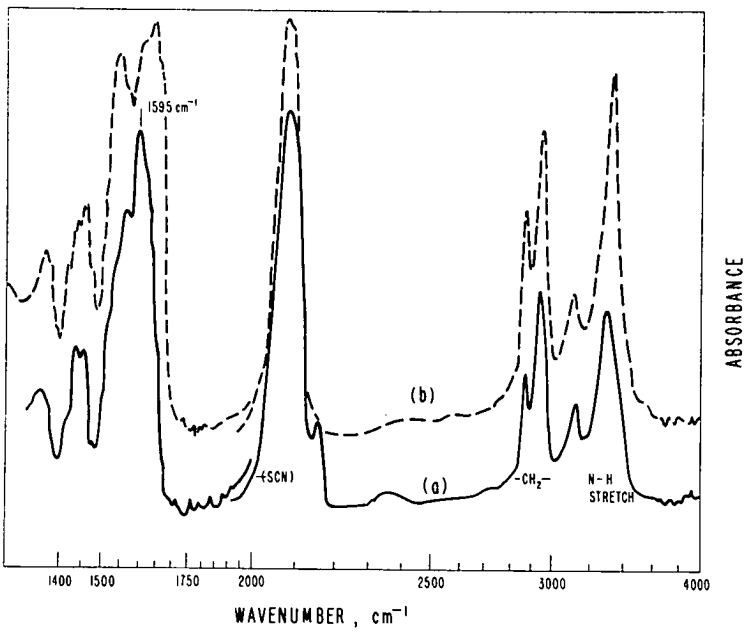


Fig. 8. Spectra of nylon 6 films treated with 30% w/v aqueous solutions of (*a*) Zn(SCN) for 60 min; (*b*) $Co(SCN)_2$ for 120 min.

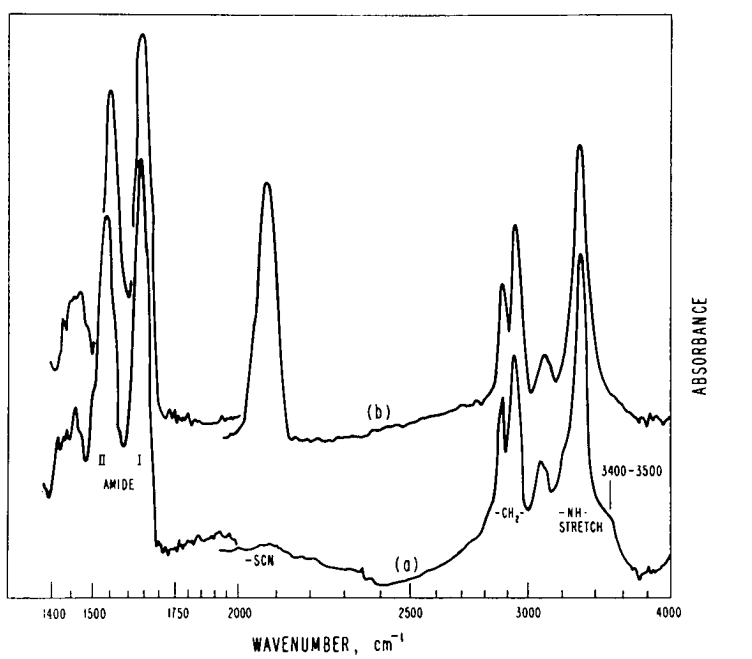


Fig. 9. Spectra of nylon 6 films treated with 30% w/v aqueous solutions of (*a*), $Ca(SCN)_2$ for 120 min; (*b*) $Ba(SCN)_2$ for 82 min.

manner similar to cast films containing lithium halides, as reported in Part II.[3]

The rate of absorption of the thiocyanates by nylon 6 was determined by measuring the optical density of the —SCN absorption at 2050 cm^{-1} (^{D}—SCN) and the optical density of the —CH absorption at 2940 cm^{-1}

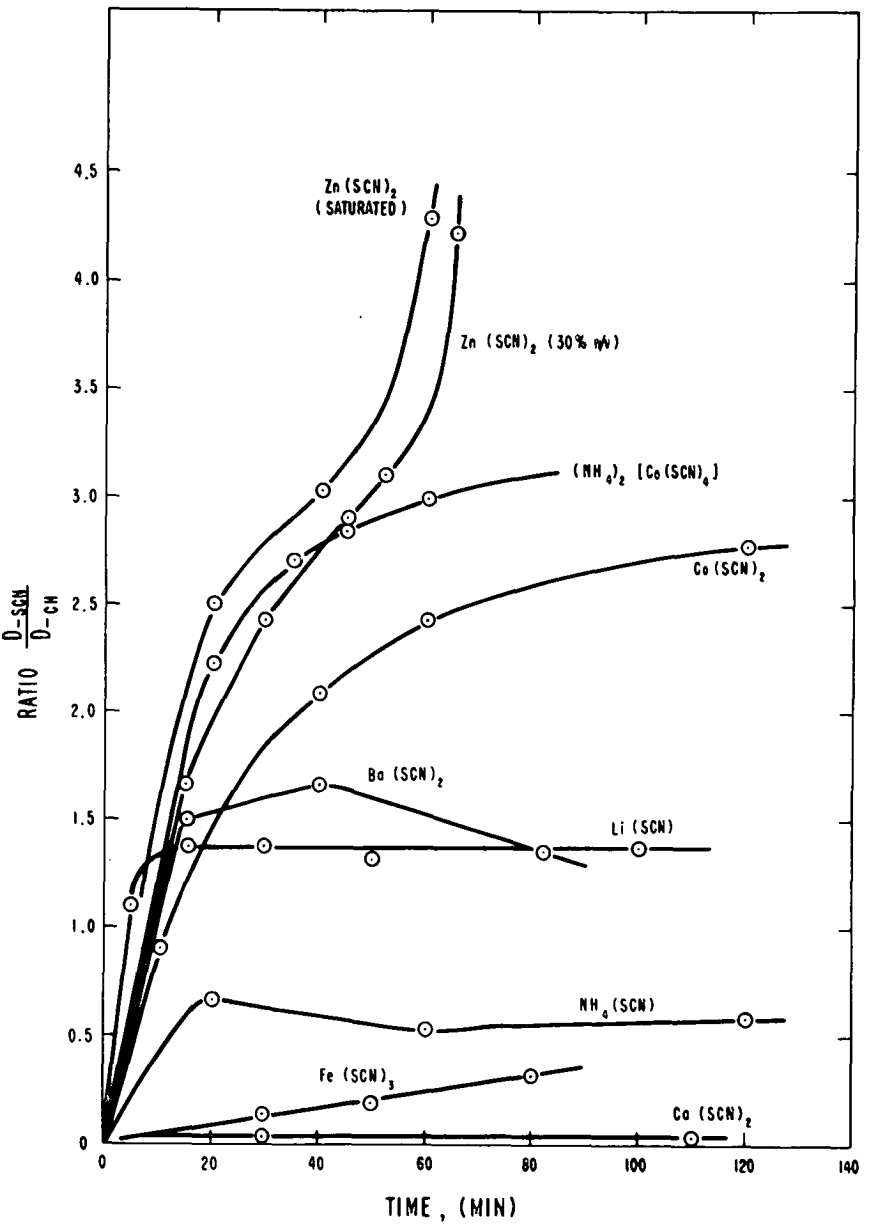


Fig. 10. The sorption of metal thiocyanates by nylon 6 film.

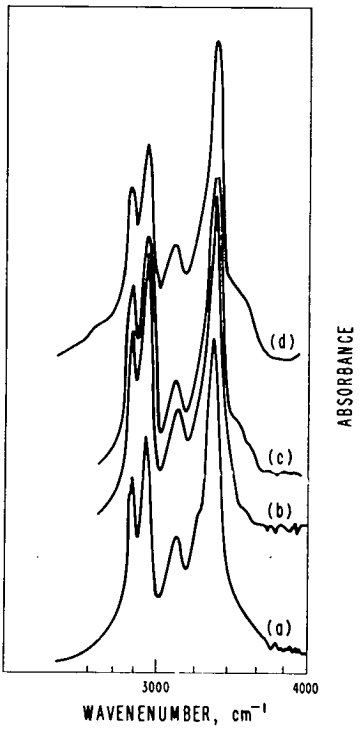


Fig. 11. Spectral changes in nylon 6 films treated with metal salts: N—H stretching band region (*a*), untreated; (*b*), treated with $Co(SCN)_2$; (*c*) treated with $Ca(SCN)_2$; (*d*), treated with LiBr.

(^{D}—CH), in films treated for various periods. The ratio, ^{D}—SCN/^{D}—CH, was used to indicate the quantity of thiocyanate absorbed per unit thickness of nylon.

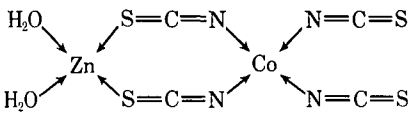
In Figure 10 values of ^{D}—SCN/^{D}—CH are plotted against time of treatment for a number of thiocyanates. Equilibrium values of ^{D}—SCN/^{D}—CH were obtained, at 21°C, within 140 min for most thiocyanates. Zinc thiocyanate was unusual and showed continued rapid absorption into nylon 6 film.

Changes in the —NH stretching band and amide II overtone band at 3060–3080 cm^{-1} were also noted in the infrared spectra of treated films, these are shown in Figure 11, for films treated with $cobalt_{II}$ thiocyanate, calcium thiocyanate and lithium bromide.

The Behavior of Cobaltothiocyanates

Ammonium cobaltothiocyanate was found to be a highly active cracking agent giving instantaneous crack initiation with nylon 6 tensile bar specimens under an applied tensile stress of 2000 psi. Crack propagation rates were also rapid being approximately 9.0×10^{-2} in./min, and total rupture

of the specimens occurred within 5 to 10 min. Potassium cobaltothiocyanate was found to be equally active. Barium cobaltothiocyanate was also an active cracking agent but crack initiation was slower and times to rupture longer. Calcium cobaltothiocyanate, like calcium thiocyanate and calcium chloride, was not active in aqueous solution but was a weak cracking agent in methanolic solution. Zinc cobaltothiocyanate was inactive in both aqueous and methanolic solution. This was an unexpected result and it is believed that in this compound the complex anion is coordinately linked to the zinc thus:



Jeffery[8] has already shown the existence of similar S → Hg bonding in mercuric cobaltothiocyanate. Coordination of this type would prevent formation of a complex with nylon. Nylon 6 films treated with ammonium and potassium cobaltothiocyanate solutions rapidly developed an intense blue colour and became soft and rubbery. The infrared spectra of these films showed no shifting of the amide I and amide II bands. Uptake of these cobaltothiocyanates by nylon 6 was rapid and the equilibrium value of ^{D}—SCN/^{D}—CH was high. In addition marked changes occurred in the

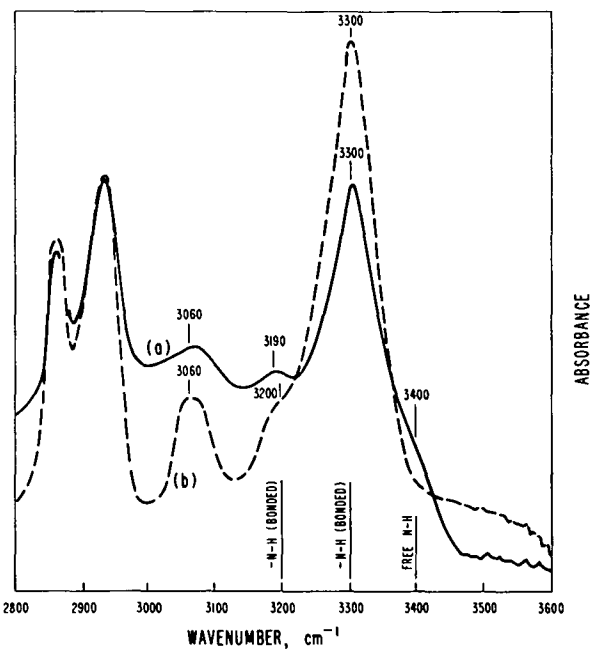


Fig. 12. Spectral changes in nylon 6 film; (*a*) treated with aqueous ammonium cobaltothiocyanate solution for 30 min; (*b*), after "reversion" on washing with hot water and drying.

N—H stretching region, similar in some respects to those previously observed in nylon 6 films treated with hydrochloric acid.[3] These changes are shown in Figure 12.

DISCUSSION

The metal thiocyanates, like the metal halides described in Part II,[3] show no uniform action on nylons.

Zinc thiocyanate and cobalt$_{II}$ thiocyanate appear to be Type I cracking agents, and act in a similar manner to the Type I halides described earlier.[3] These agents are believed to form complexes with the amide groups of the nylon. In the complex the metal ion is coordinately linked to the carbonyl oxygen atom of the nylon and inter-amide group hydrogen bonding is no longer possible. These agents are characterised by their very rapid absorption by the nylon, their rapid rupture of nylon 6 films at low stresses and their rapid crack initiation and rupture of stressed nylon 6 tensile bar specimens.

Calcium, lithium and barium thiocyanates appear to act as Type II cracking agents similarly to the Type II halides previously described.[3] With these agents hydrogen bonding between the solvated metal ion and the carbonyl oxygen atom of the amide group appears to occur, effectively destroying interchain hydrogen bonding in the polyamide. These agents can be effective solvents for nylons, their solvent power being determined by the acid strength of the solvated metal ion. Lithium thiocyanate in aqueous solution is a very powerful solvent for nylon 6, similar to lithium bromide, and causes very rapid crack propagation in stressed nylon 6 by simple solvent cracking. Ammonium, potassium and ferric thiocyanates are weak cracking agents for nylon 6 giving slow crack initiation and very slow absorption of the metal salt with low equilibrium values for ^{D}—SCN/^{D}—CH. These agents are believed to bring about stress cracking by simple ionic interference with the interchain hydrogen bonding in the polyamide.

The equilibrium values of ^{D}—SCN/^{D}—CH are of interest as they may indicate the ability of the thiocyanates to be absorbed by rendering the nylon 6 more amorphous. Wood and King[9] have shown, by deuteration studies, that only a limited quantity of nylon 6 is accessable to deuterium oxide, and is capable of being deuterated. This proportion has been identified with amorphous regions in the polymer. These same regions are also believed to be accessable to water, while the crystalline regions are not. The low equilibrium thiocyanate absorption values observed with calcium, ammonium and ferric thiocyanate (^{D}—SCN/^{D}—CH; 0.04, 0.55 and 0.35, respectively) may reflect the absorption of these solutions by the normal amorphous regions in the polymer. The higher equilibrium values observed with the Type II thiocyanates, such as lithium thiocyanate, ^{D}—SCN/^{D}—CH 1.35 and barium thiocyanate, ^{D}—SCN/^{D}—CH, 1.5 are believed to be due to increased absorption of the solutions, as a result of the reagent rendering the polymer more amorphous. The very high values for the

Type I reagents, such as zinc thiocyanate, ^{D}—SCN/^{D}—CH, 4.0+ and cobalt$_{II}$ thiocyanate, ^{D}—SCN/^{D}—CH, 3.0+ represent the very high absorption of solution, resulting from amorphous polymer regions being created as a result of complex formation.

Some cobaltothiocyanates are active cracking agents but do not appear to act as Type I agents. This is not unexpected since in these compounds the cobalt$_{II}$ atom is fully coordinated in the anion. These agents are believed to interfere with hydrogen bonding between polymer chains by simple ionic charge effects.

The spectra of nylon 6 films treated with calcium and barium thiocyanate and ammonium cobaltothiocyanate show only minor absorbance above 3300 cm^{-1} (Fig. 11 and 12). This is probably due to a very low contribution from free N—H stretching in the presence of the solvent.

We believe, from the stress cracking parameters and infrared data, that metal thiocyanates and corresponding metal halides promote stress cracking in polyamides by similar mechanisms.

The assistance of Dr. A. G. Moritz of these Laboratories in determining the NMR spectra and helping with the interpretation of the NMR and infrared spectra is gratefully acknowledged.

References

1. P. Dunn, A. J. C. Hall, and T. Norris, *Nature*, **195**, 1092 (1962).
2. P. Dunn and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, No. 8 (1969).
3. P. Dunn and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, No. 8 (1969).
4. C. D. Weiske, *Kunststoffe*, **54**, 626 (1964).
5. D. S. Barmby and G. King, *Proc. Int. Wool Text. Res. Conf.* (Australia), B-139 (1955).
6. G. Sarda and N. Peacock, *Nature*, **200**, 67 (1963).
7. R. J. Roark, *Formulae for Stress and Strain*, McGraw-Hill, 1954, p. 223, New York.
8. J. W. Jeffery, *Nature*, **159**, 610 (1947).
9. F. Wood and G. King, *J. Text. Inst.*, **54**, T111 (1963).

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The Stress Cracking of Polyamides by Metal Salts. Part IV. Metal Nitrates

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Synopsis

The stress cracking of polyamide (nylon 6) by a number of metal nitrates in aqueous and nonaqueous solution has been investigated. Copper and zinc nitrates were the most active. Stress cracking parameters were determined and the sorption of the nitrates into nylon 6 film was studied using infrared techniques. Evidence of coordination of some metal nitrates when sorbed into nylon 6 was obtained.

INTRODUCTION

In earlier parts of this work we have described the action[1–3] of metal halides, thiocyanates, and cobaltothiocyanates on polyamide (nylon) materials. In part I it was briefly noted that lithium nitrate in methanolic solution was a weakly active stress cracking agent. In this paper, part IV, the behavior of a number of metal nitrates on nylon 6 is described.

EXPERIMENTAL

Materials

Nylon 6 extruded sheet (Trogamid B, Dyanamit-Nobel A.G., Troisdorf, Germany) and 0.001-in.-thick extruded, blown, unplasticized nylon 6 film as described in our earlier work[1–3] were again employed as standard materials.

Techniques

The stress cracking parameters, time to crack initiation (ΔT) and crack propagation rate (K) as defined in part I[1] were determined using tensile bar specimens. The stressed film technique described in part III[3] was employed to determine critical stress data.

Infrared spectra of nylon 6 films treated with metal nitrates were obtained using a Beckman IR 8 spectrophotometer by means of the techniques described earlier in parts II[2] and III.[3]

RESULTS

Qualitative Determination of Activity

Using simple evaluation trials, saturated aqueous and methanolic solutions of Cu(II), Zn, Co(II), Ni(II), Ca, Mg, and Li nitrates in contact with

TABLE I
Crack Propagation Data of Metal Salt Solutions[a]

	Aqueous saturated solution						Methanolic saturated solution			
	4000 psi		2000 psi		400 psi		4000 psi		2000 psi	
Metal salt	ΔT, min	K, in./min	ΔT, min	K, in./min	ΔT, min	K, in./min	ΔT, min	K, in./min	ΔT, min	K, in./min
$Cu(NO_3)_2$	instant	1.2×10^{-2}	instant	0.4×10^{-2}	instant	0.1×10^{-2}	instant	2.0×10^{-4}	40.0	2.2×10^{-4}
$Zn(NO_3)_2$	instant	0.1×10^{-3}	instant	0.8×10^{-4}	0.1	$<0.5 \times 10^{-4}$	instant	0.5×10^{-4}	0.1	2.6×10^{-5}
$Co(NO_3)_2$	instant	0.8×10^{-4}	instant	$<0.5 \times 10^{-4}$	0.2	$<0.5 \times 10^{-4}$	instant	$<0.5 \times 10^{-4}$	0.2	$<0.5 \times 10^{-4}$
$Ni(NO_3)_2$	instant	0.5×10^{-4}	instant	$<0.5 \times 10^{-4}$	1.0	$<0.5 \times 10^{-4}$	instant	$<0.5 \times 10^{-4}$	0.2	$<0.5 \times 10^{-4}$
$Mg(NO_3)_2$	instant	$<0.5 \times 10^{-4}$	instant	$<0.5 \times 10^{-4}$	1.0	$<0.5 \times 10^{-4}$	instant	2.5×10^{-4}	0.2	0.6×10^{-4}
$Ca(NO_3)_2$	instant	$<0.5 \times 10^{-4}$	instant	$<0.5 \times 10^{-4}$	1.0	$<0.5 \times 10^{-4}$	instant	1.7×10^{-4}	0.2	0.5×10^{-4}
$ZnCl_2$	instant	1.7×10^{-2}	instant	0.6×10^{-2}	0.1	0.3×10^{-2}	instant	0.5×10^{-1}	instant	0.3×10^{-1}

[a] Conditions: nylon 6 specimens, water content 3.5%, at 21°C.

stressed specimens of nylon 6 were found to be active agents, in that cracking was initiated at tensile stresses of 2000 psi, or less in some cases. Only one salt, lithium nitrate, was found to be inactive in aqueous solution, while all the metal nitrates were active in methanolic solution. In comparative trials, aqueous and methanolic solutions of the corresponding acetates and sulfates were found to be inactive.

Stress Cracking Parameters

The parameters, time to crack initiation (ΔT) and crack propagation rate (K), for various saturated aqueous and methanolic solutions of nitrates are shown in Table I. From these results it appears that only copper(II) nitrate is very active as a stress cracking agent, and this salt has an activity of the same order as that of 80% aqueous zinc chloride solutions previously described.

Critical stress data for the rupture of stressed nylon 6 films by 1*M* solutions of the nitrates tend to confirm these results and are shown in Table II.

TABLE II
Activity of Solutions of Metal Nitrates on Stressed Nylon 6 Films[a]

Metal nitrate in solution[b]	Time to rupture film, sec			
	5100 psi	4900 psi	4700 psi	4500 psi
$Cu(NO_3)_2$	6	31	266	>3600
$Ni(NO_3)_2$	23	97	1380	>366
$Co(NO_3)_2$	50	153	>3600	—
$Zn(NO_3)_2$	125	117	>3600	—
$Mg(NO_3)_2$	191	1000	>3600	—
$Ca(NO_3)_2$	232	1180	>3600	—

[a] Conditions: nylon 6 film, 0.001 in., water content 3.5%, at 21°C. The yield stress of the film as determined by a tensometer was 5310 psi for specimens cut parallel to the direction of extrusion.[3]

[b] Using a 1.0 *M* aqueous solution.

TABLE III
Infrared Data on Nylon 6 Film Treated with Metal Nitrates

Metal nitrate	Sorption value[a]	Nitrate absorption band		Crack propagation rate
		position, cm^{-1}	shift, cm^{-1}	in./min (at 2000 psi)
Cu(II)	1.308	1290	−80	4.0×10^{-3}
Zn	0.641	1296	−81	8.6×10^{-5}
Co(II)	0.475	1300	−72	1.0×10^{-5}
Ni(II)	0.246	1305	−78	s[b]
Mg	0.137	1332	−18	s[b]
Ca	0.058	1332	−18	s[b]

[a] The measure of sorption is the ratio of the absorbance of the nitrate band at the frequency shown and the C—H band of nylon 6 at 2940 cm^{-1} (D_{NO_3}/D_{CH}), after treatment for 90 min.

[b] Crack initiation occurred but crack propagation was extremely slow, that is, less than 1.0×10^{-6} in./min.

The activity of the metal nitrates is in the order

$$Cu(II) > Zn > Co(II) > Ni(II) > Mg > Ca > Li$$

and, with the exception of the nitrates of Mg, Ca, and Li, all were more active in aqueous solution than in methanolic solution.

The correlation between stress cracking activity and the rate of absorption of the active salts, which was previously demonstrated for metal thiocyanates,[3] is also shown by the metal nitrates. Data showing this correlation are given in Table III.

Effects of Sorption of Nitrates on Infrared Spectra

Nylon 6 films were treated with metal nitrates by immersing the films in aqueous saturated solutions of the salts for various periods of time. As described for the metal thiocyanates,[3] the sorption of the nitrate was followed by measuring the optical density of both the nitrate infrared absorp-

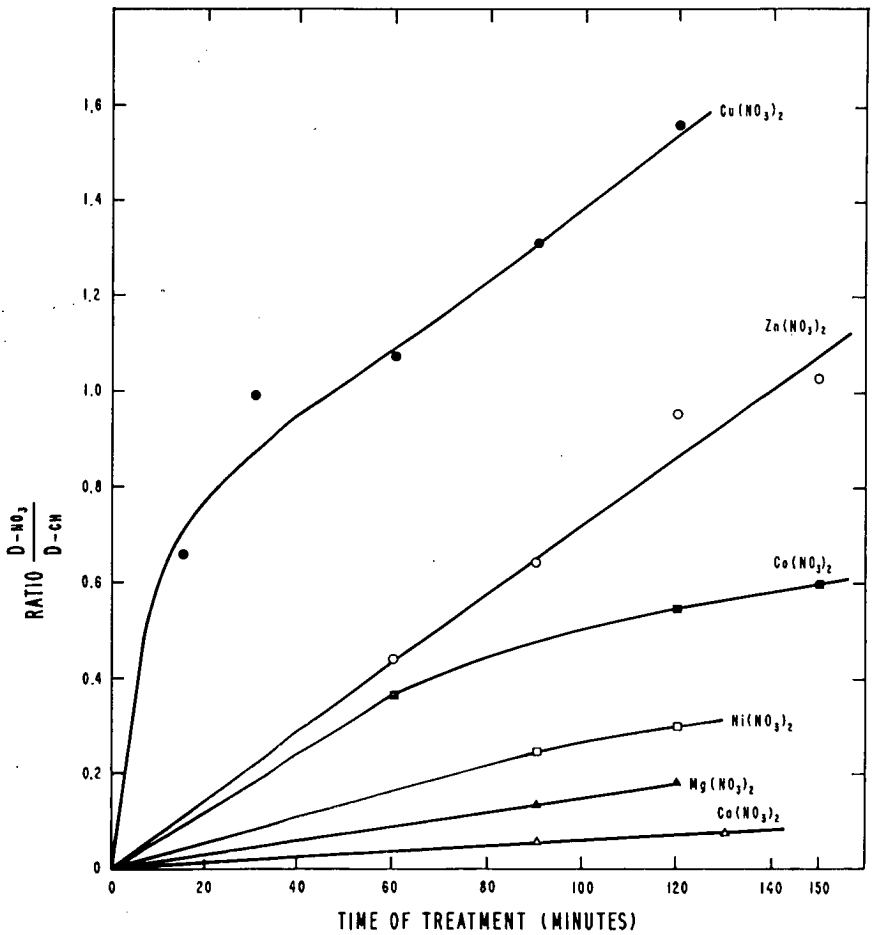

Fig. 1. Sorption of metal nitrates by nylon 6 film.

tion band and the nylon 6 C—H absorption band at 2940 cm^{-1}. Curves showing the sorption of the various nitrates into nylon 6 film are shown in Figure 1.

Spectra of nylon 6 films treated with copper(II) nitrate and zinc nitrate showed the development of a new absorbance band (Fig. 2) at 1590 cm^{-1},

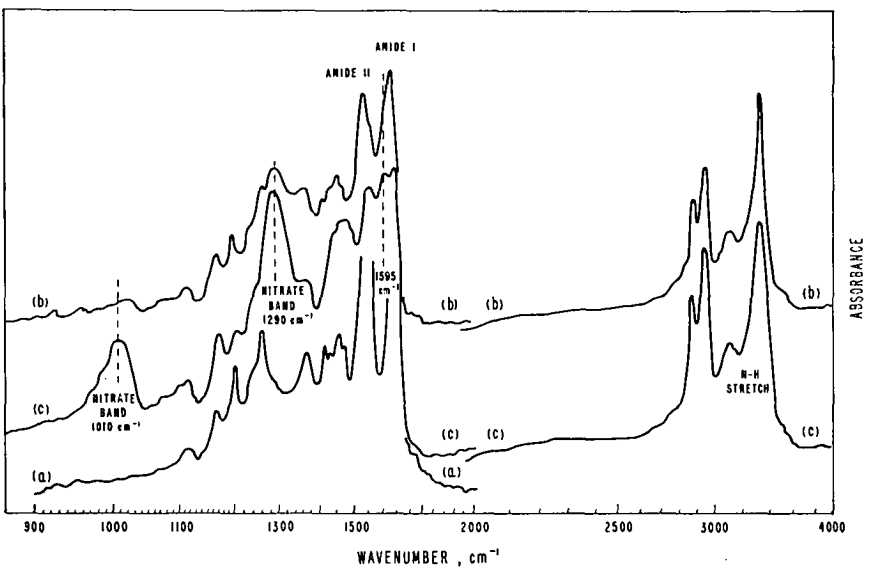

Fig. 2. Spectral changes in nylon 6 films treated with metal nitrates: (*a*) untreated; (*b*) treated with $Zn(NO_3)_2$ for 90 min; (*c*) treated with $Cu(NO_3)_2$ for 90 min.

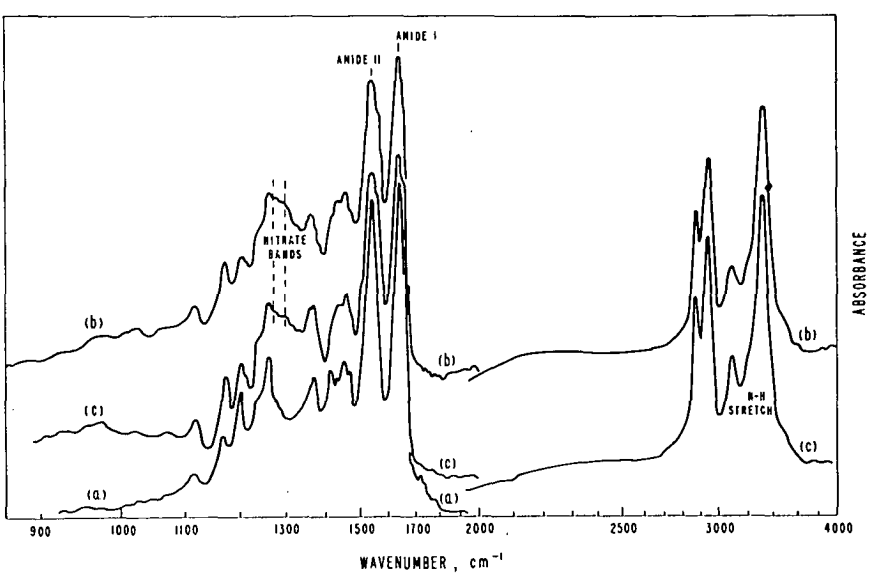

Fig. 3. Spectral changes in nylon 6 films treated with metal nitrates: (a) untreated; (*b*) treated with $Co(NO_3)_2$ for 60 min; (*c*) treated with $Ni(NO_3)_2$ for 90 min.

TABLE IV
Infrared Data on Nylon 6 Films Treated with Metal Nitrates

Nylon 6 film treatment[a]	Amide I band		Amide II band		Amide II overtone		New band
	Position, cm^{-1}	Shift, cm^{-1}	Position, cm^{-1}	Shift, cm^{-1}	Position, cm^{-1}	Shift, cm^{-1}	Position, cm^{-1}
Untreated nylon 6	1637	Nil	1537	nil	3080	nil	—
Copper(II) nitrate	1630	−7	1560	+23	3120	+40	1595
Zinc nitrate	1630	−7	1555	+18	3110	+30	1610
Cobalt(II) nitrate	1635	−2	1550	+13	3100	+20	1595[b]
Nickel(II) nitrate	1635	−2	1545	+8	3100	+20	1595[b]
Magnesium nitrate	1640	+3	1535	−2	3085	+5	—
Calcium nitrate	1640	+3	1540	+3	3085	+5	—

[a] Treated with saturated solutions at room temperature.
[b] Approximate position of shoulder.

which we have previously shown[2] is characteristic of certain agents designated as Type I metal salts. Other active metal salts which do not produce this characteristic absorption band have been designated as Type II. With the other Type I nitrates, this is less noticeable but is shown for nickel(II) nitrate and cobalt(II) nitrate in Figure 3. Characteristic shifts of the amide I, amide II, and amide II overtone bands were also noted and are tabulated in Table IV.

Also noted was a marked shift of the nitrate absorbance band, as shown in Table III, to a position consistent with the NO_2—O→M coordinated form. This occurred in nylon films treated with the Type I nitrates of Cu(II), Zn, Co(II), and Ni(II).

With the Type II nitrates of Mg, Ca, and Li, this effect was not noted and only minor shifts of the nitrate band occurred.

DISCUSSION

The infrared spectra of solid metal nitrates and of metal nitrates in tributyl phosphate (TBP) solution have been compared with the spectra of the same nitrates in aqueous solution by Katzin,[4] who concluded that in the nonaqueous solvent the nitrate ions are coordinated by the cation and that a similar interaction exists in the crystalline state for many metal nitrates.

We have found that the nitrate infrared absorption bands due to sorbed nitrates of Type I metal cations in polyamide (nylon 6) films correspond to the bands shown by such coordinated nitrates in nonaqueous solution and in the crystalline state. This is shown in Table V by the data for $Cu(NO_3)_2$ comparing reported infrared bands by Katzin,[4] Miller and Wilkins,[5] and Mathieu and Lounsbury[6] with our own spectral data. In each case the reported main band is italicized.

In the crystalline state, $Cu(NO_3)_2$ is reported[5] to be uncoordinated and to have its major band at 1378 cm^{-1}. In tributyl phosphate solution it is coordinated and has its major band shifted to 1285 cm^{-1}. Thus it would appear that copper nitrate is also coordinated when sorbed into nylon 6 film because the major nitrate band occurs at 1290 cm^{-1}. There is no evidence that copper nitrate exists in coordinated form in saturated aqueous solution.[6]

TABLE V
Infrared Absorption Bands of Copper Nitrate

Nitrate form	Nitrate absorption band
$Cu(NO_3)_2 \cdot 3H_2O$, crystalline[4]	836 cm^{-1}, *1378 cm^{-1}*, 1587 cm^{-1}, 1790 cm^{-1}
$Cu(NO_3)_2$, in TBP solution[4]	*1285 cm^{-1}*, 1495 cm^{-1}, 1543 cm^{-1}
$Cu(NO_3)_2$, saturated aqueous solution[6]	719 cm^{-1}, 1024 cm^{-1}, 1048 cm^{-1}, 1315 cm^{-1}, 1405 cm^{-1}, 1480 cm^{-1}
$Cu(NO_3)_2$, sorbed in nylon 6	746 cm^{-1}, 807 cm^{-1} 1010 cm^{-1}, *1290 cm^{-1}*

Similarly, the observed shifts of the major nitrate bands on zinc nitrate, cobalt(II) nitrate and nickel(II) nitrate (Table III) indicate that when sorbed into nylon 6 these nitrates are also present in the coordinated form.

It thus appears that nitrates of Type I metal cations, when sorbed into nylon 6 films, become coordinated by the cation despite their noncoordinated state in the aqueous solution from which they are sorbed. However, nitrates of the Type II cations remain uncoordinated on sorption into the nylon. This result is not unexpected in light of the previously proposed structures of complexes formed by Type I and Type II metal salts with polyamides[2] and is strong confirmation that coordination of the cation is usual with Type I cations, but not with Type II cations, in their interaction with polyamides.

References

1. P. Dunn and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, 1641 (1969).
2. P. Dunn, and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, 1657 (1969).
3. P. Dunn, and G. F. Sansom, *J. Appl. Polym. Sci.*, **13**, 1673 (1969).
4. L. I. Katzin, *J. Inorg. Nucl. Chem.*, **24**, 245 (1962).
5. F. A. Miller, and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).
6. J. P. Mathieu, and M. Lounsbury, *Dis. Faraday Soc.*, **9**, 196 (1950).

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APPENDIX 17 APPLICATIONS RESULTING FROM STRESS CRACKING INVESTIGATIONS

17a The Surface Treatment of Nylons for Adhesive Bonding.
P. DUNN and G.F. SANSOM.
Preprint issued for AUSPLAS 69 Conference. The Plastics Institute of Australia, Sydney, 1969. 17.2 - 17.7

17b Bonding of Nylon *(Ultramid)*. Technical data sheet issued by *BASF Australia Ltd*, 1971. 17.8

APPENDIX 17a

The Surface Treatment of Nylons for Adhesive Bonding

P. DUNN and G. F. SANSOM

Defence Standards Laboratories

P. DUNN G.F. SANSOM

Semi crystalline polyamide (nylon) materials are stress cracked by aqueous and non-aqueous solutions of metal salts. Such solutions are a little-known but severe environmental hazard for nylons. The solutions chemically modify the structure of the nylon, and using infra-red and n.m.r. spectroscopic techniques, two separate mechanisms, depending on the metal salt, have been elucidated. Both mechanisms however, result in preferential swelling and solution of the amorphous regions of the polymer and as a result it is possible to use these metal salt solutions to etch nylon. Stereoscan electron micrographs of etched surfaces show that numerous micro-pits and cavities, often with undercut structure are present on surfaces etched in this way. Such a surface provides an excellent physical key for adhesive bonding and the adhesion of surface finishes.

Nylon 6 surfaces etched with solution of such salts gave adhesive bond strengths up to 300% greater than those achieved with unetched surfaces with a wide range of adhesives. Similarly etched surfaces gave improved adhesion of laquers and the flex crack resistance of laquered surfaces was improved by an order of magnitude. The currently recommended etching treatments for nylon surfaces involve phenolic or acid reagents. Using metal salt solutions etching can be carried out without the use of these hazardous materials.

Using coloured complex metal salts, the reaction between polyamides and metal salts can be employed to give simple positive identification of nylons 6, 66 and with special pretreatments higher nylons.

In addition, because of the rapidity of stress crack initiation and crack propagation with metal solutions, such solutions can be used under controlled conditions to semi-quantitatively determine the level of stresses in moulded nylon components.

Introduction

Because of their attractive chemical and physical properties, nylons are today finding a wide range of applications, including many in all types of military equipment. Several years ago, a case moulded from olive-drab nylon 6 was specified for use in an Army portable field telephone. After some time severe cracking and delamination of the nylon 6 case adjacent to the battery compartment was noticed in prototypes under-going field trials.

The failures varied from fine cracks in the surface to serious delamination of the mouldings, or to complete disintegration. The investigation of this failure has been described in full in a DSL report (1). It was established that these failures were due to stress cracking associated with zinc chloride electrolyte which had leaked from discharged dry cells and this proved to be consistant with an earlier observation, reported by Ensanian (2), of cracking of nylon in the presence of zinc powder and hydrochloric acid.

Figure 1 shows typical stress cracking of a telephone case moulding induced by spotting the surface with an 80% zinc chloride solution.

Investigation of the action of zinc chloride solutions showed that the rate and degree of cracking were dependent on the temperature, the concentration of the solution, the water content of the nylon and the level of stress in the sample. High values of all these parameters favoured rapid crack initiation and propagation. Telephone cases moulded from nylon 11 were found to be resistant to zinc chloride solutions.

Stress Cracking by Metal Salts

Following these initial observations the stress cracking of nylons by a number of metal salts in aqueous and non-aqueous solutions was investigated systematically.

Earlier workers had reported isolated instances of the action of inorganic materials on nylons. Weiske (3) has described the stress cracking of dry nylons by a number of solvents and noted the action of methanolic solutions of calcium chloride. Barmby and King (4) have shown that both silk and nylons are soluble in arsenic and antimony trichlorides with little apparent molecular chain degradation, and that silk precipitated from aqueous lithium bromide solution is similar to silk precipitated from solution in antimony trichloride. Sarda and Peacock (5) have shown that lithium bromide and lithium and magnesium perchlorates in aqueous solution reduce the modulus properties of nylons 6 and 66 and also bring about modifications of the infrared spectra of these polyamides.

As a result of our systematic investigation it was found that many metal chlorides, bromides, iodides, thiocyanates, perchlorates and nitrates were active stress cracking agents whilst the corresponding acetates and sulphates were inactive. Investigation of the cracking process itself showed that with these agents crack initiation, and crack propagation were both stress dependant quantities, and that at high stresses almost instantaneous crack initiation could occur with crack propagation rates of up to 1 inch per minute.

These cracking parameters were found to be independent of the surface geometry of the nylon and the hydrogen ion concentration of the cracking agent. It was also determined that, although the intrinsic viscosity of nylons in formic acid solution was slightly lower in the presence of zinc chloride, no change occurred on standing and that therefore the stress cracking was not due to hydrolysis or metal ion catalysed hydrolysis of the nylon.

Mechanics of Stress Cracking

l salts which are active stress cracking agents, induce ristic changes in the infra red spectra of both nylon nide model compounds. These changes and their tation have been described in our recent work (6) e enabled the mechanism of the stress cracking o be elucidated. Two types of changes have been l depending on the metal salt involved, and on this e metal salts have been classified as Type I or Type spectral changes appear to be due to the formation plexes between the amide group and the metal salt, ctures for these complexes have been proposed. alts, for example, active salts of zinc, copper$_{II}$, , form complexes in which the metal atom is co-or- linked to the carbonyl oxygen atom of the amide Figure 2A). These agents cause stress cracking by ence with hydrogen bonding within the polyamide sticisation.

· II metal compounds, for example active salts of calcium, magnesium etc. in solution in some solvents otondonating solvated species which act as direct for polyamides in a manner similar to phenols and acid. Type II agents appear therefore to cause simple cracking. (Figure 2B).

lon films treated with metal thiocyanates and it is possible to quantitatively measure the rate of of the salt by measurements of the intensity of the nate and nitrate infra red absorption bands. It has monstrated that those salts which are more rapidly d and which give higher equilibrium sorption values most active stress cracking agents. In Table I the ion of the salt and the crack propogation rates of iocyanates and nitrates are compared.

rt, Markowski and Jeschke (7) have described a ism of environmental stress cracking in which sol- other liquids or vapours capable of being absorbed lymer, cause swelling of the polymer and induce localised stresses which cause crack initiation. lasticisation' of amorphous regions and crack propo- long crystallite boundaries in semi crystalline poly- e also important factors in the cracking process. In king of nylons by metal salts absorption occurs in the amorphous regions, although on long contact e active agent the crystalline regions are also attacked polymers become increasingly amorphous.

Effect of Crystallinity

importance of crystallinity and crystallite size in the of nylon can be clearly shown by the following ental results. The effect of higher crystallinity by orientation was investigated by determination racking parameters of nylon 6 tensile bar specimens ly cold drawn to various elongations from the origi- lition. After cold drawing, these specimens were at a constant tensile stress of 4000 psi and the crack n and rupture in the presence of zinc chloride solu- idied. The results shown graphically in Figures 3, 4 w both time to crack initiation and time to rupture with increasing elongation on cold drawing Speci- ld drawn beyond 200% failed to show any crack n after 6000 minutes.

ncrease in crystallinity of nylon 6 on cold drawing n described by Muller and Pfluger (8) who have hat in cold drawn nylon 6 a density increase from 1.14 occurs, corresponding to an 8% increase in crys- . These results confirm that rapid stress cracking of y metal salt solutions occurs as a result of rapid n of the active agent into the amorphous regions of mer and that with increasing crystallinity sorption of the reagent is reduced and the stress cracking slowed.

On the basis of these results it was expected that the newer nucleated grades of nylon 6 and 66 of higher crystallinity, should have superior resistance to stress cracking by metal salts. A comparison of the stress cracking resistance of nucleated and unnucleated nylon 66 has been carried out and the results in fact show that both crack initiation and crack propagation were more rapid in the nucleated material (Table 2.). Perhaps the level of crystallinity is not as important as the available crystallite boundary area, which is certainly expected to be greater in the nucleated microcrystalline material.

Stress Cracking of Mouldings

The typical pattern of cracking obtained when a few drops of zinc chloride solution are placed at random on the surface of an injection moulded article involves gross destructive delamination of the moulding. The cracking appears to initiate and extend, at first, perpendicular to the surface for a very short distance, and then rapidly changes direction until propagation is almost parallel to the surface.

A number of factors are believed to be responsible for this behaviour. In injection moulded items rapid cooling of the melt occurs at the surface of die; inner layers of the moulding cooling more slowly. As a result the 'skin' of the nylon moulding tends to be more amorphous and less mould shrinkage occurs in this 'skin'. Higher shrinkage in the more crystalline material underneath induces a stressed skin effect in the moulded item. Following treatment with an active solution rapid absorption occurs in the 'skin' region causing preferential swelling strains which are relieved by delamination.

Photomicrographs of the fracture surfaces obtained during delamination clearly show how propagating cracks have skirted the boundaries of orientated regions resulting from flow processes during the injection moulding giving a pattern of nearly parallel ridges.

Applications

The behaviour of metal salts toward nylons can be usefully applied.

Firstly, because of the extremely rapid absorption of the complex salts ammonium cobaltothiocyanate and potassium cobaltothiocyanate and the resultant blue colour imparted to the polyamide, nylon materials may be conveniently and rapidly identified by a simple test. If nylon 6 or 66 are immersed in a mixed solution of potassium or ammonium thiocyanate and cobaltous chloride, they are rapidly coloured blue by absorbed cobaltothiocyanate, whilst polyesters, polyacetals and other similar materials are not affected. Special pretreatments are required to enable this test to distinguish higher nylons.

Secondly, provided a calibration curve is available giving crack initiation time, as a function of stress, for a particular nylon material at constant temperature, an approximate value of the level of stress in injection moulded components can be obtained by determination of the crack initiation time, at the same temperature, of components tested with the same active agent. Applying this technique to moulded items brought to our attention we have often determined moulded-in stresses of the order of 4000 – 5000 psi to be present in injection moulded articles. Articles having very low internal stresses do not show any cracking at all. We have found, for example, using 80% aqueous zinc chloride as a cracking agent that for nylon 6 there is a critical stress level of about 1000 psi below which crack initiation is very slow.

Metal Salts as Etching Agents

However, it is as etching agents for nylons, that these solutions show most interest. If nylon with stresses below

the critical level is immersed in active solutions at temperature up to 50°C for periods up to 60 minutes and then washed, a fine microetched surface can be obtained. Photographs of these surfaces obtained by 'Steroscan' electron microscopy show innumerable small pits and cavities in the surface often with undercuts which can provide an excellent physical key for adhesive bonding and or organic finishes. Figures 5, 6 and 7 show this clearly.

In our experimental work nylon specimens were etched by immersion in active solutions for periods of 15 to 60 minutes at various temperatures then thoroughly washed with water and allowed to dry. After such treatment specimens were lap bonded with various adhesives or laquered and tested. The adhesive bond shear strength was determined using a Hounsfield Tensometer with a jaw separation rate of 1/16 inch per minute. The adhesion of laquer to the nylon was assessed by measuring the flex cracking resistance of laquered specimens, using a Ross Flexometer (9).

The etching agents investigated were aqueous solutions of zinc chloride, lithium bromide, zinc thiocyanate, cupric nitrate, and magnesium perchlorate and methanolic solutions of zinc chloride and lithium bromide.

Initial trials with zinc chloride solution etched nylon 6 specimens using an epoxy-polyamide adhesive and a cyanoacrylate adhesive (Eastman 910) showed that the shear strength of the lap joint was greater with etched nylon 6 and that specimens immersed in the etching agent at room temperature for 60 minutes gave higher values than specimens immersed for only 15 minutes. These results are shown in Table 3. Temperature of the etching medium was found to be not significantly important in determining the final shear strength of the bond and this is also shown in Table 3.

The comparative activity of a number of etching agents is shown in Table 4. Generally, the aqueous etching agents were more effective and the best results were obtained with solutions of zinc chloride, cupric nitrate and magnesium perchlorate.

With a number of epoxy adhesive formulations improvement of bond shear strengths were shown to be variable, with results depending very much on the epoxy formulation and etching agent used. However with some combinations high bond shear strength could be obtained. The bond shear strengths of some 24 adhesive/etching agent combinations are given in Table 5.

The results obtained in bonding etched nylon to aluminium and other metal substrates were generally less improved.

The treatment of nylon 6 with metal salts solutions was also found to give improved adhesion of lacquers and the flex-cracking resistance of laquered nylon surfaces is shown in Table 6. The currently recommended etching treatments for nylon surfaces prior to adhesive bonding involve the use of phenolic or formic acid based etching agents. Where phenolic based adhesives i.e. (resorcinol-formaldehyde) are employed, pre-etching of the nylon surface is ommitted because of the etching nature of the adhesive. In bonding nylon to nylon the solvent action of phenols and formic acid is also employed in simple solvent bonding techniques. In addition improved bonding of nylon to nylon can be achieved with a range of adhesives using aqueous solutions of selected metal salts as etching agents instead of the more hazardous phenolic or acid reagents.

REFERENCE

1. Dunn, P., Liggins, T. and Norris, T., D.S.L. Report No. 300 (1968).
2. Ensanian, M., Nature, 193, 161 (1962).
3. Weiske, C.D. Kunststoffe, 54, 626 (1964).
4. Barmby, D.S. and King, G., Proc. Int. Tax. Res. Conf. (Australia), B–139, (1955).
5. Sarda, G. and Peacock, N., Nature, 200, 67 (1963).
6. Dunn, P. and Sansom, G. F., to be published in Journal of Applied Polymer Science.
7. Stuart, H.A., Markowski, G. and Jeschke, D., Kunststoffe, 54, 618 (1964).
8. Muller, A. and Pfluger, R., Plastics, 350, (1959).
9. ASTM D–1052 (1965), "Resistance of Vulcanised Rubber or Synthetic Elastomers to cut growth by the use of the Ross Flexing Machine". American Society for Testing and Materials, Philadelphia Pa. Samples 0.040 inch thick were used, in the unnotched condition.

TABLE 1

HE SORPTION OF NITRATES AND THIOCYANATE BY NYLON 6

Salt	Sorption*	Crack Propagation Rate Inches/Min. @ 2000 psi
Nitrate	1.31	400 x 10^{-5}
Nitrate	0.64	3.6 x 10^{-5}
Nitrate	0.47	0.5 x 10^{-5}
Nitrate	0.25	+
Nitrate	0.14	+
Nitrate	0.06	+
Thiocyanate	4.5	1200 x 10^{-5}
Thiocyanate	2.6	130 x 10^{-5}
Thiocyanate	0.4	50 x 10^{-5}
Thiocyanate	< 0.1	**

Ratio absorbances of nitrate or thiocyanate band to nylon CH band @ 2940 cm^{-1}.

Crack initiation occurred very slowly, crack propagation rates < 1 x 10^{-6}.

No crack initiation occurred.

TABLE 2

MPARISON OF RUPTURE OF NUCLEATED AND UNNU-EATED NYLON 66 BY 80% AQUEOUS ZINC CHLORIDE

erial	Density	Crystal* -linity	Times to Rupture (Minutes)	
			@ 3200 psi	@ 2000 psi
ndard'	1.14	0.3	115	278
			107	450
			120	435
			255	425
			102	412
			Mean 140	Mean 400
eated'	1.15	0.4	25	138
			45	105
			43	190
			15	242
			65	275
			Mean 38	Mean 190

$= \frac{d - da}{dk - da}$ (A. Muller, R. Pfluger, Plastics, Sept.1959, p 350)

d = Density of specimen
da = 'Amorphous' density (1.09)
dk = 'Crystalline' density (1.24)

TABLE 3

CT OF ZINC CHLORIDE ETCHING ON THE ADHESIVE D STRENGTH OF VARIOUS ADHESIVES WITH NYLON

hesive	BOND SHEAR STRENGTH P.S.I.				
	Untreated nylon	Treated with aqueous 80% ZNC12 solution.			
		Room Temp. 20°C		Room Temp. 50°C	
		15 min.	60 min.	15 min.	60 min.
y – amide 1	113	184	277	200	280
oa te 2	163	279	321	280	320
act sive 3	81	100	117		

'Epikote' 828, 100 p.b.w., 'Synolid' 960, 60 p.b.w.
'Eastman' 910.
'Bostik' 1177.

TABLE 4

EFFECT OF VARIOUS ETCHING AGENTS ON BOND STRENGTH

Etching Solution	BOND SHEAR STRENGTH p.s.i.	
	Epoxy–Polyamide 1 Bonded	Cyanoacrylate 2. Bonded
None (controls)	113	221
80% Aqueous $ZnCl_2$	277	335
Satd Methanolic $ZnCl_2$	174	178
Satd Aqueous LiBr	215	367
Satd Methanolic LiCl	242	231
Satd Aqueous $Zn(SCN)_2$	233	558
Satd Aqueous $Cu(NO_3)_2$	320	260
Satd Aqueous $Mg(ClO_4)_2$	383	423

1. 'Epikote' 828: 'Synolid' 960, (100:60)
2. 'Eastman' 910.

TABLE 5

EPOXY ADHESIVE BOND STRENGTHS OF ETCHED NYLON

Epoxy Adhesive	Bond shear strength, p.s.i.			
	Untreated	Etched with salt solution		
		Aqueous $Mg(ClO_4)_2$	Aqueous $(Cu(NO_3)_2$	Aqueous $ZnCl_2$
1	166	440	317	272
2	185	351	213	187
3	185	370	215	341
4	262	443	577	489
5	207	407	546	455
6	271	447	580	485
7	119	290	224	203
8	137	407	149	335

Key to Adhesives.

1. 'Epikote' 828 /'Synolid' 960 100:60
2. 'Araldite' AY108/HY 956 100:16
3. " AY103/HV 953U 100:100
4. " AY105/HV 953U 100:100
5. " AW106/HV 953U 100:80
6. " AW106/HV 953U 100:80
7. " AY103/'Versamid' 125, 100:60
8. " AY105/Versamid' 125, 100:60

TABLE 6

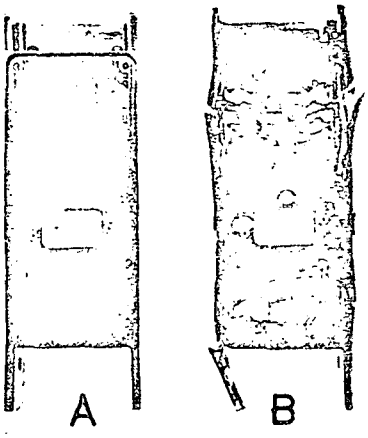
RESISTANCE OF LACQUERED NYLON SURFACES TO FLEXING

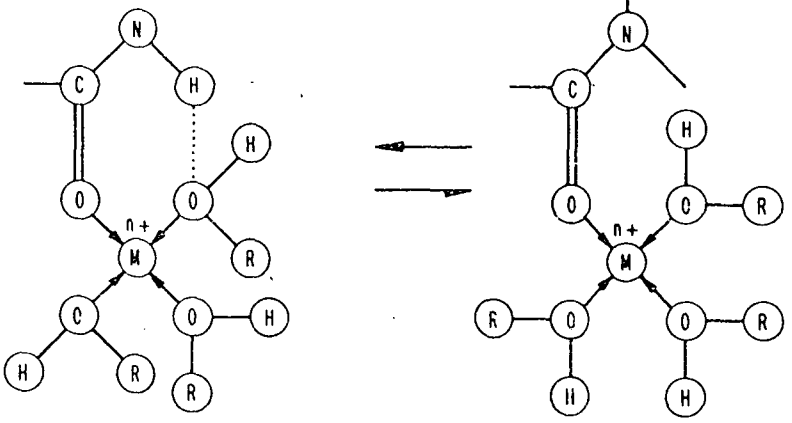
Etching treatment prior to laquering*	No. of flexes to cracking of laquer film.			Mean
	1	2	3	
Untreated	1,500	1,800	4,000	3,650
Aqueous 80% $ZnCl_2$	>200,000	>240,000	>200,000	>200,000
Satd. Methanolic $ZnCl_2$	>200,000	>240,000	>240,000	>200,000
Satd. Aqueous Zn $(SCN)_2$	>200,000	>240,000	>240,000	>200,000
Satd. Aqueous Cu $(NO_3)_2$	11,050	31,350	8,700	17,000
Satd. Aqueous Mg $(ClO_4)_2$	>150,000	>150,000	>240,000	>150,000
Satd. Methanolic LiCl	2,200	2,400	4,300	3,000

* The lacquer used was a standard commercial product recommended for use in nylon, and was applied according to the manufacturers instructions.

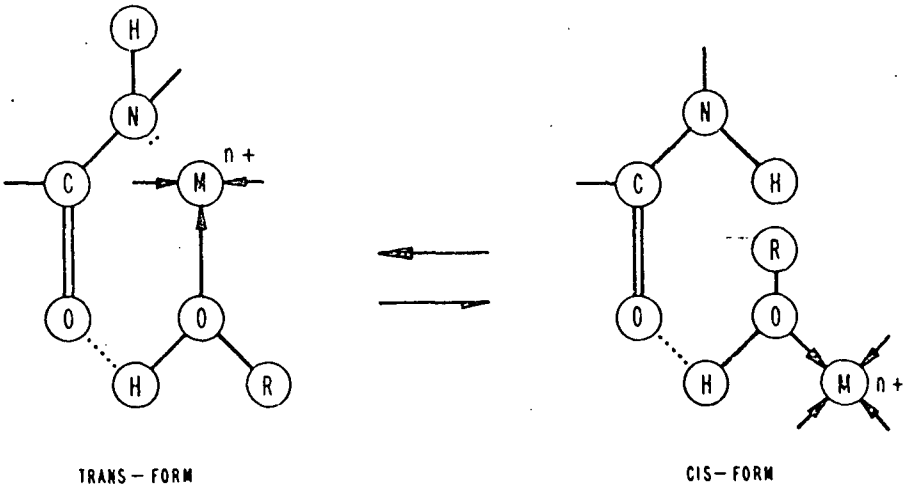
STRUCTURES OF COMPLEXES

1. Moulded Telephone Set 'K', stress cracked by 80% aqueous zinc chloride solution.



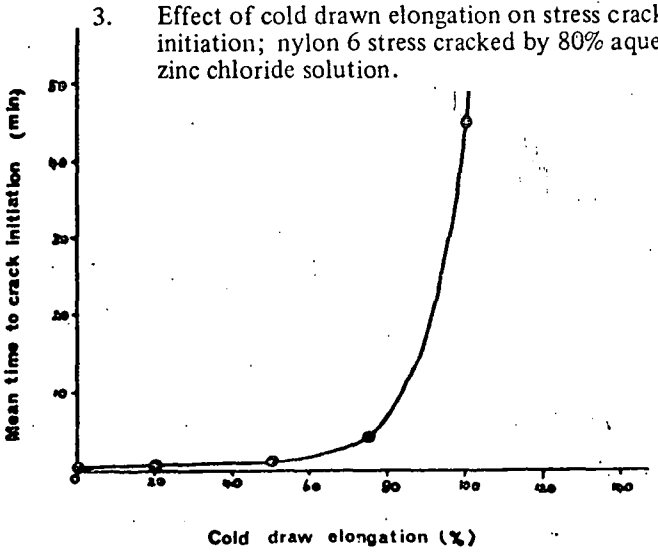


(A) 2a. Proposed structure for complex between amide group and Type I metal salt.

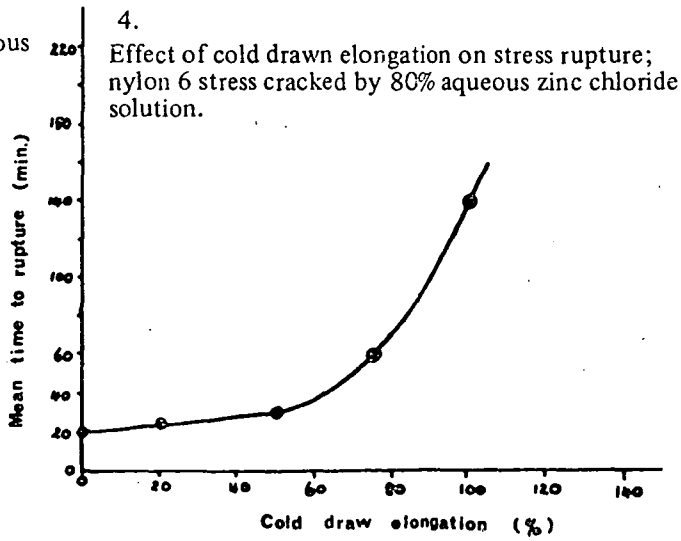


(B) 2b. Proposed structure for complex between amide group and Type II metal salt.

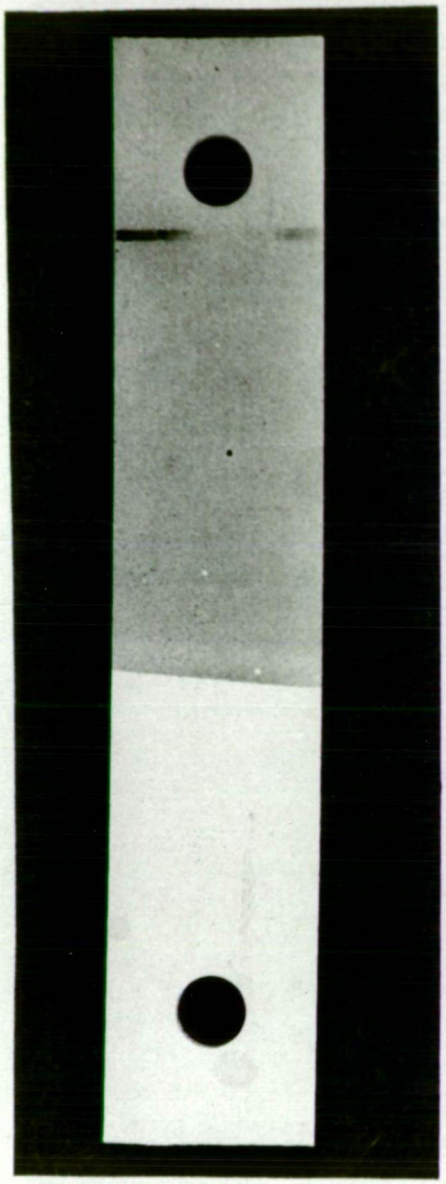
3. Effect of cold drawn elongation on stress crack initiation; nylon 6 stress cracked by 80% aqueous zinc chloride solution.

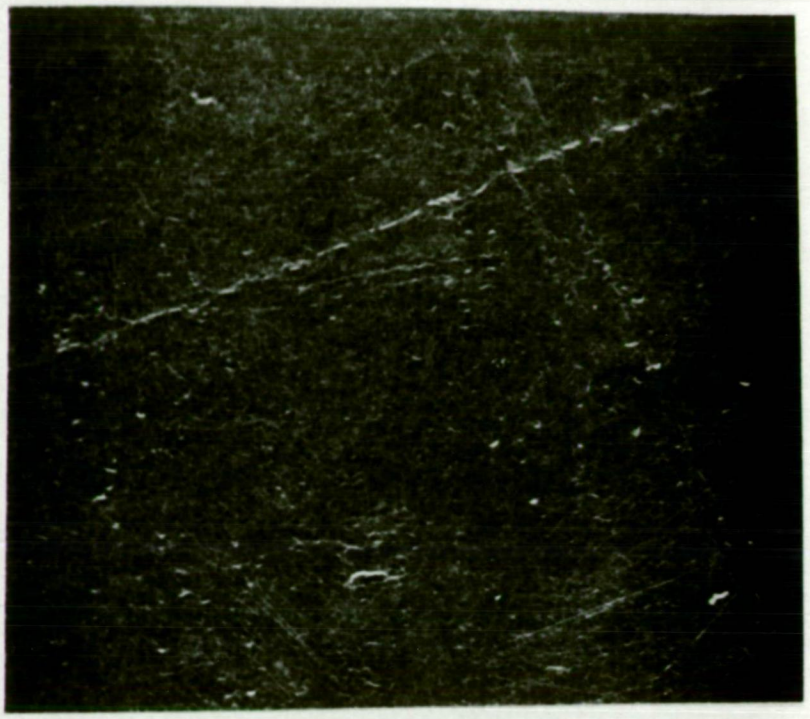


4. Effect of cold drawn elongation on stress rupture; nylon 6 stress cracked by 80% aqueous zinc chloride solution.

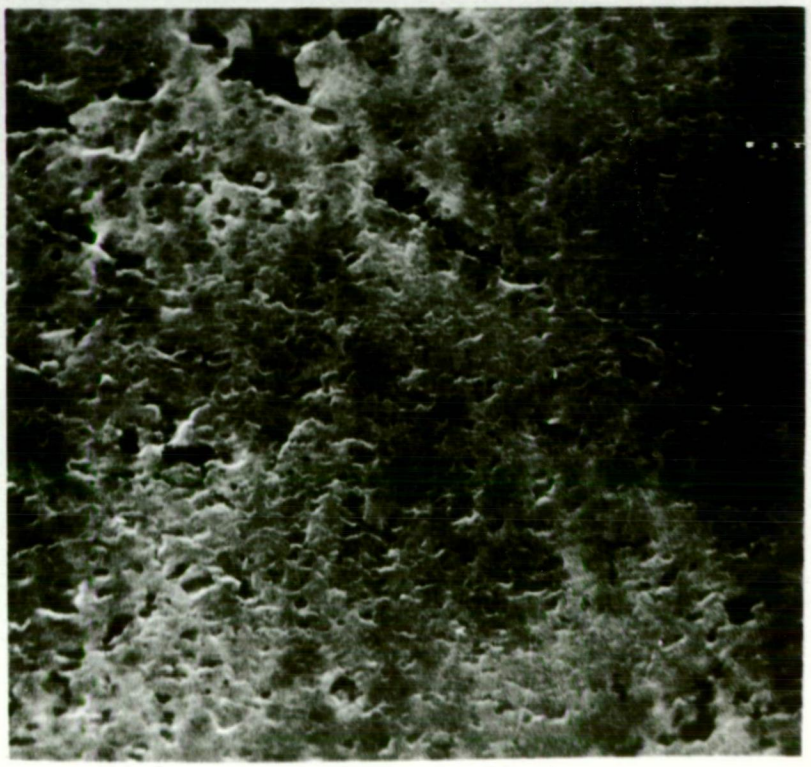


5. Nylon 6 etched by 80% aqueous zinc chloride, 15 minutes treatment at 50°C.





6. Electron micrograph of unetched nylon 6 surface X2,400.



7. Electron micrograph of nylon 6 surface etched by 80% aqueous zinc chloride solution, 15 minutes treatment at 50°C x 2,400.

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Technical Information

BONDING OF ULTRAMID

June 1971

An adhesive solution for the bonding of nylon can be made in the following manner:-

Mix 20 parts by weight Calcium Chloride
75 " " " Methanol (Technical Grade)
5 " " " Water

Add to this 5-10 parts Ultramid IC
or Ultramid B3 and mix for some hours.

The Ultramid should be powdered to shorten solution time.

Apply to the area to be bonded, repeat after a few minutes, then place together and fix the bond until it is dry (about 1 day).

This method is claimed to give bonds of a welded form.

.....

In presenting this information, we cannot claim to serve in any but an advisory capacity and we can undertake no liability. All recommendations regarding the use of our products should be modified, if necessary, to conform with local conditions and materials employed.

NO. 444
RC/JM

3 17/12.

APPENDIX 18 NEW SEALS FOR NYLON COMPONENTS

18a Formulation Details for Ethylene-Propylene Copolymer Rubbers 18.2 - 18.3

18b Test Data and Specification Requirements for Ethylene - Propylene Rubbers 18.4 - 18.6

The information listed at Appendix 18a is a retype of Table 13, reference 230, and in Appendix 18b is a retype of Appendix 1 of the same reference. The cover and contents pages of reference 230 are given at Appendix 15d (p.15.5).

COMPOUND NUMBER D.S.L. 500 SERIES	500 F	500 Q	502 H
Dutral N (45±4, ML 1+4(100°C)), EPR	100	-	-
Dutral P (20±4, ML 1+4(100°C)), EPR	-	100	100
Sulphur	0.4	0.4	0.4
Acarb HAF Carbon black	50	-	-
Acarb FEF Carbon black	-	100	30
Atla 60 process oil	-	-	10
Dicup R (Dicumyl peroxide)	4	4.5	4
Activator OC (Triallyl cyanurate)	-	-	1
	154.4	204.9	145.4
Press Cure (min/°C)	10/180	10/180	10/180
Hardness, IRHD	65	82	43
Compression Set, % (24 h at 70°C under 25% compression)	5.9	6.0	12.0
Performance tests on electrical switch diaphragms			
(a) Ballooning	Satisfactory	Satisfactory	-
(b) Sealing	Satisfactory(1)	Satisfactory(1)	-
(c) Differential pressure test, in. of mercury; 6 min	10	-	-
(d) Storage at -20°C	Satisfactory after 70 h	Fails after 70 h	-

COMPOUND NUMBER D.S.L. 500 SERIES	500 F	500 Q	502 H
(e) Storage at +70°C	Satisfactory after 28 days	Satisfactory after 11 days	-
<u>Performance tests on main case seal</u>			
Sealing efficiency after storage at -20°C, ambient and +70°C	-	-	Satisfactory

(1) Modified clamp plate required.

APPENDIX 18b

TEST DATA AND SPECIFICATION REQUIREMENTS FOR ETHYLENE - PROPYLENE RUBBERS

1. VULCANISATE PROPERTIES

COMPOUND NO.	DSL 500F* REQUIREMENTS	DSL 500F* TYPICAL TEST FIGURES	DSL 502H* REQUIREMENTS	DSL 502H* TYPICAL TEST FIGURES
Specific Gravity (1)	1.050 ± 0.015	1.052	1.000 ± 0.015	1.003
Original Hardness (2)	65 ± 3	65	43 ± 3	43
Original Tensile Strength, lb/sq.in. (3)	2300 min	2770	1000 min	1430
Original Elongation at Break, %	250 min	360	450 min	540
Compression Set, % (4) (24 h in air at 120°C)	20 max	14	25 max	21
Resistance to Air-ageing (5) (48 h at 120°C)				
Change in Hardness, Degrees (2)	+ 6 max	+ 2	+ 6 max	+ 2
Change in Tensile Strength, %	- 10 max	+ 4	- 10 max	- 0.7
Change in Elongation at Break, %	- 15 max	- 8	- 10 max	- 3.7
Volume Loss, % (6)	2 max	1.3	3.5 max	2.2
180° Bend Test (7)	No cracking	Conformed	No cracking	Conformed

COMPOUND NO.	DSL 500F*		DSL 502H*	
	REQUIREMENTS	TYPICAL TEST FIGURES	REQUIREMENTS	TYPICAL TEST FIGURES
Resistance to Swelling in Tritolyl Phosphate (8) (48 h in T.T.P. at 150°C)				
Change in Hardness, Degrees (2)	- 10 max	- 7	- 5 max	0
Change in Volume, % (6)	+ 15 max	+ 11	+ 8 max	+ 4.3
180° Bend Test	No cracking	Conformed	No cracking	Conformed
Surface condition of test-piece	No tackiness or surface disintegration	Conformed	No tackiness or surface disintegration	Conformed

* For formulations, see APPENDIX 18a

2. TEST METHODS

(1)	Specific Gravity	:	B.S.903, Part A1, Method A
(2)	Hardness : (International Rubber Hardness Degrees)	:	B.S.903, Part A7 Determined on a composite sample, of approx. 5/16 in. thickness.
(3)	Tensile Strength and Elongation at Break	:	B.S.903, Part A2, Die D
(4)	Compression Set	:	B.S.903, Part A6, Method A using a Type 1 specimen
(5)	Resistance to Air-ageing	:	B.S.903, Part A12, Method B
(6)	Resistance to swelling in tritolyl phosphate (T.T.P.) and volume loss on air-ageing	:	B.S.903, Part A16, Method A
(7)	180° Bend Test	:	A test-piece which has been used for volume and hardness change determination shall be bent double around a 0.075 in. diameter steel mandrel and shall show no cracking of the stressed surface.
(8)	Tritolyl Phosphate Test Fluid	:	Shall conform generally with British Standard 1999 (1957).

APPENDIX 19 SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPDM) RUBBERS

19a Silica-Reinforced Ethylene-Propylene Diene (EPDM) Rubbers
PETER DUNN AND VINCENT S. JAVIER
Technical Report C and OM-7. US Army Natick Laboratories, US Army Materiel Command, Natick, Massachusetts, USA. 19.2 - 19.54

19b Coloured EPDM Compounds - Laboratory Records 30 September, 1964 and Formulations 19.55 - 19.59

19c Properties of EPDM Rubbers after Indoor Ageing 19.60 - 19.61

Specimens of EPDM vulcanizates produced as part of this programme, are located at Appendix 28.

APPENDIX 19a

TECHNICAL REPORT
C&OM-7

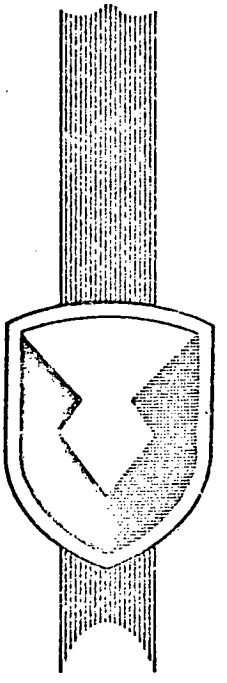
SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPD) RUBBERS

by

Peter Dunn

Vincent S. Javier

CLOTHING & ORGANIC MATERIALS DIVISION



August 1965

U. S. Army Materiel Command
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts

TECHNICAL REPORT

C&OM-7

SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPD) RUBBERS

by

PETER DUNN

and

VINCENT S. JAVIER

Rubber, Plastics, and Leather Engineering Branch
CLOTHING & ORGANIC MATERIALS DIVISION

Project Reference:
50305101

August 1965

U. S. Army Materiel Command

U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts

FOREWORD

The Armed Services have a continuing need for high quality black and non-black rubber vulcanizates for military use. These low-cost general purpose rubbers should be capable of use over the temperature range from -50°C to +150°C and should have good long-term ozone, aging, and weathering resistance. The properties of the recently discovered ethylene-propylene diene (EPD) rubbers indicate that these materials could be suitable for many military requirements. Although EPD rubbers reinforced with carbon black have been extensively investigated, little work has been reported on high quality non-black EPD rubbers. The object of this project is to determine the properties of non-black EPD rubber vulcanizates and to evaluate their military potential.

This research was performed in the Rubber, Plastics, and Leather Engineering Branch, Clothing and Organic Materials Division, U. S. Army Natick Laboratories, Natick, Massachusetts, between May 1964 and March 1965. The research chemists assigned to the project were Mr. Peter Dunn and Mr. Vincent S. Javier. Mr. Dunn is employed at the Defence Standards Laboratories, Department of Supply, Melbourne, Australia. His research at the U. S. Army Natick Laboratories was sponsored by the Australian Government.

S. J. KENNEDY
Director
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Approved:

DALE H. SIELING, Ph.D.
Scientific Director

W. W. VAUGHAN
Brigadier General, USA
Commanding

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ABSTRACT

High quality ethylene-propylene diene (EPD) rubber vulcanizates can be produced by using hydrated silica as the reinforcing filler. Modification of EPD rubber by chemical promotors such as p-quinone dioxime and the use of silica activators such as polyethylene glycol gives compounds with an acceptable rate of cure. Hot mastication, especially in the presence of halogenated compounds, gives vulcanizates with good physical properties. Processing aids such as stearic acid may be used, and oil-extended EPD rubber is a convenient plasticizer for silica-reinforced compounds.

To reduce costs, silica fillers can be extended with other such low-cost fillers as hard clay. EPD rubbers may also be blended with other elastomers. High quality silica-reinforced expanded EPD rubbers may be produced by conventional blowing agents and processing techniques. Silica-reinforced EPD rubbers crosslinked with organic peroxides give vulcanizates with good resistance to abrasion and compression set.

EPD rubber vulcanizates have excellent resistance to ozone and fungi and, in the presence of ultraviolet screening agents, show good weathering properties. It is expected that, in the future, ethylene-propylene diene rubbers will have many applications in military equipment.

SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPD) RUBBERS

I. Introduction

Ethylene-propylene diene (EPD) rubber is a terpolymer of ethylene, propylene, and an unconjugated diene. It differs from ethylene-propylene copolymer rubber (EPR) in that the pendant unsaturation introduced by the diene monomer enables the rubber to be crosslinked by conventional sulphur vulcanizing techniques as well as by organic peroxides.

Although EPD rubber did not become commercially available until 1964, extensive compounding studies using carbon black fillers have already been undertaken and McCabe[1] has reviewed the five-year outlook for EPD rubber in the United States. EPD rubber is a high-performance, low-cost, general-purpose rubber which can be compounded to give vulcanizates with good resistance to heat, ozone, water, steam, acids, alkalis, alcohols, glycols, and phosphate esters. The vulcanizates have excellent electrical and dynamic properties as well as good resistance to aging and weathering. Because of these attractive properties, the U. S. Army Materiel Command is investigating the use of EPD rubber in applications such as coatings for synthetic fabrics[2], protective masks[3,4], and tank track pads[5]. It has also undertaken processing studies[6].

In the presence of strongly reinforcing fillers, such as carbon black[7], EPD rubbers yield vulcanizates of high modulus and tensile strength. In many applications where low cost, non-black color, or good electrical resistance is required, it is necessary to use mineral fillers. However, poorly reinforcing mineral fillers and amorphous EPD rubber yield vulcanizates which generally do not have the excellent stress-strain properties of compounds reinforced with carbon black.

This report describes the use of fine-particle-size silica as a non-black reinforcing filler for EPD rubber. It discusses the physical properties of these vulcanizates (which are excellent) and the potential use of silica-reinforced EPD rubbers in military equipment.

II. Materials

A. Commercially Available EPD Rubbers

At present, EPD rubbers are available from three major chemical companies in the United States. Details of the rubbers and their properties are given in Table I. In general, these data were obtained from the manufacturers' literature[8,9,10,11]. Each manufacturer uses a specific diene monomer, the type and amount of which has a marked effect on the processing and curing characteristics of the formulated compound.

Table I

PROPERTIES OF COMMERCIAL ETHYLENE-PROPYLENE DIENE RUBBERS PRODUCED IN THE USA

Trade Name	Nordel 1040	Nordel 1070	Nordel 1070E	Nordel 1145	Royalene 200	Royalene X300	Royalene X301	Royalene X400	Enjay 3509
Manufacturer	du Pont	du Pont	du Pont	du Pont	US Rubber	US Rubber	US Rubber	US Rubber	Enjay Chemical
Type	100% EPDR	100% EPDR	Oil-extended Oil: 50phr(1)	100% EPDR (Extrusion Grade)	100% EPDR	100% EPDR	100% EPDR	Oil-extended Oil: 100phr(1)	100% EPDR
Physical form	Slab(2)	Slab	Slab	Slab	Chips	Chips	Chips	Elastic crumb	Chips
Color and odor(3)	Amber	Amber	Dark amber	Amber to Light grey	Light amber	Light amber	Light amber	Light amber	Light amber
Standard package, lb	75	75	75	75	50	50	50	50	50
Ethylene, wt, %	53(4)	53(4)	53(4) phr	-	-	-	-	-	55
Diene monomer	1:4 Hexane-diene type	1:4 Hexane-diene type	1:4 Hexane-diene type	1:4 Hexane-diene type	Dicyclopen-tadiene type	Dicyclopen-tadiene type	Dicyclopen-tadiene type	Dicyclopen-tadiene type	Methylene nor-bornene type
Unsaturation, wt, %	2-3	2-3	2-3	2-3	2-3	2-3	2-3	2-3 phr	2.6
Iodine no.(g/100 g)	-	-	-	-	10	12	12	-	-
Ash, wt, %	-	-	-	-	-	-	-	-	0.3
Volatiles, wt, % (24 hr/100°C)	0.7	0.7	0.7	0.7	-	-	0.6	0.6	0.3
Stabilizer, wt, %	-	-	-	-	0.5	1.0	1.0	1.0 phr	0.25(5)
Specific gravity	0.85	0.85	0.88	0.85	0.865	0.865	0.865	0.897	0.86
Cost, cents per lb	30	30	-	30	30	30	30	20	30
Refractive index	1.481-1.484	1.481-1.484	-	1.481-1.484	-	-	-	-	-
Coefficient of linear expansion, $(°C)^{-1}$	2.3×10^{-4}	2.3×10^{-4}	-	2.3×10^{-4}	-	-	-	-	1.6×10^{-4}
Intrinsic viscosity	2.5-2.7(6)	-	-	-	-	-	-	-	2.7-3.3(7)
Mooney viscosity ML(1 + 4)									
212°F	48	80	36	63	140	130	60	60	87
250°F	40	70	30	45	-	-	52	70	62

Notes:
(1) Naphthenic process oil
(2) Exhibits some cold flow
(3) No significant odor present
(4) Ref. 11
(5) Parabar 441, Enjay Chemical Company. A non-staining butylated hydroxy toluene
(6) At 25°C: 0.1% solution in tetrachloroethylene (w/v)
(7) At 135°C: 1.0% solution in decalin (w/v)

B. Silica Reinforcing Fillers

Among the mineral fillers, such as hard and soft clays, whitings, talcs, silicates, and aluminates, that have been evaluated as reinforcing fillers for EPD rubbers[8,9,10,12,13], only fine-particle-size silicas have a reinforcing effect equal to that of carbon black. The review by Bachmann and coworkers[14] describes the properties and reinforcing action of the commercially available silicas and silicates.

In the United States, one low-cost readily available precipitated hydrated silica of very fine ultimate particle size is Hi-Sil 233[15]. A compacted form is available as Hi-Sil 215[16]. Bartrug and Meltz[17] have shown that Hi-Sil 233 can be used to produce high quality, non-black EP rubber vulcanizates. At the Natick Laboratories, we used Hi-Sil 233 as the reinforcing filler for EPD rubber vulcanizates.

C. Miscellaneous Compounding Materials

The compounding materials used were commercial products obtained from recognized suppliers[18]. Details are given in Appendixes I and II. Other compounding materials comparable in chemical composition and activity should prove to be equally satisfactory.

III. Experimental

All of the rubber compounds were processed on conventional rubber compounding equipment. Whenever possible, rubber masterbatches were mixed on a 20- by 10-inch variable-speed two-roll mill, while hot mixing and final compounding were carried out on 12- by 6-inch two-roll mills. Test sheets were vulcanized in 4-cavity chrome-plated molds in a steam-heated press.

Standard testing equipment was used. The test methods are listed in Appendix III.

Outdoor exposure tests were carried out at Natick where samples were exposed facing south at an angle of 45°. Water leaching, accelerated weatherometer exposures, and soil burials were undertaken by the United States Testing Company at Hoboken, New Jersey. These vulcanizates were returned to the Natick Laboratories for evaluation.

IV. Results and Discussion

A. Curing Systems for Silica-Reinforced EPD Rubbers

1. Sulphur systems

In EPD rubbers, the level of unsaturation selected allows vulcanization with a variety of curing systems commonly used with other

general purpose elastomers. As the level of unsaturation of EPD rubbers is similar to that found in butyl rubber, the sulphur and accelerator combinations suitable for curing butyl are also generally effective with the EPD rubbers. Combinations of sulphur with such accelerators as thiuram disulphide and dithiocarbamates will vulcanize EPD rubber when used in conjunction with thiazole-type compounds. Organic peroxides[24] and phenolic resins[21,25] are also effective crosslinking agents. Natta and coworkers[19], Auda and coworkers[20,21], Roche[22], and others[7,8,9,10,23,29] have discussed the selection of a suitable sulphur-type curing system for carbon black and mineral-filled EPD rubbers.

Curing systems based on zinc oxide, sulphur, tetramethylene thiuram tetrasulphide (TMTD), dipentamethylenethiuram tetrasulphide (DPMTT), and mercaptobenzothiazole (MBT) give satisfactory bloom-free vulcanizates. Those based on DPMTT are known to give vulcanizates with good heat resistance also[26,27]. On the other hand, vulcanizates with non-sulphur crosslinkages obtained from resin, quinoid, and peroxide curing systems display maximum heat- and compression-set resistance.

For the development of tensile properties, the optimum sulphur level of the curing system was found to be 2 phr. This generally gave the maximum degree of crosslinking, as assessed by the highest stress at 300 percent elongation and the lowest ultimate elongation. Higher levels of sulphur caused excessive bloom while lower levels tended to decrease the state of cure.

The optimum time and temperature for curing commercial EPD rubbers with zinc oxide (5 phr), sulphur (2 phr), TMTD (0.75 phr), DPMTT (0.75 phr), and MBT (1.5 phr) was found to be 20 minutes at 160°C. This gave bloom-free vulcanizates with good physical properties. Longer cure times gave vulcanizates with improved compression set, modulus, and abrasion resistance, and with no tendency to reversion. Curing systems based on zinc dimethyl dithiocarbamate (ZDC) may be used with EPD rubber[8,9,10,22], but many of these vulcanizates show a marked tendency to bloom.

The properties of vulcanizates based on Nordel 1040 and Enjay 3509 are given in Table II. Royalene EPD rubbers can be compounded to give vulcanizates with equivalent physical properties using other curing systems[10]. The presence of either dioctyl sebacate or a naphthenic oil plasticizer does not markedly affect the activity of the curing system (Section IV, B3).

2. Effect of "ultra" accelerators

In order to develop EPD compounds with a fast rate of cure, "ultra" accelerators such as metal- containing dithiocarbamates may be used. Copper dimethyl dithiocarbamate or tellurium diethyl dithiocarbamate are

TABLE II

EFFECT OF EPD RUBBER TYPE ON VULCANIZATE PROPERTIES

Compound	1	2	3	4
Formulation*:				
Nordel 1040 EPD rubber	100	-	80	-
Enjay 3509 EPD rubber	-	100	-	80
Royalene X400 EPD rubber	-	-	40**	40**
Dioctyl sebacate	20	20	-	-
Tensile strength, psi	3100	2700	3300	3275
Ultimate elongation, %	600	530	540	570
Stress at 300% elongation, psi	1000	1150	1200	1200
Hardness, Shore "A"	64	61	62	63
Abrasive index, NBS	210	283	275	286
Compression set, %, after				
24 hr at room temperature	14.3	11.7	8.6	11.9
24 hr at 100°C	71.0	67.7	71.0	73.3
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	300	250	200	70

*Formulation: EPD rubber and dioctyl sebacate as listed; Hi-Sil 233, 50; polyethylene glycol 4000, 1; stearic acid, 1; p-quinone dioxime, 1; chlorosulphonated polyethylene 7.5; HAF black, 3. Compounds 1 and 3 hot-milled 10 min at 160°C; compounds 2 and 4 hot-milled 5 min at 160°C.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds cured 20 min at 160°C.

**Equivalent to 20 phr of EPD rubber and 20 phr of naphthenic oil.

effective accelerators for EPD rubbers. While their color precludes their use in light colored stocks, they can be used in olive-drab EPD rubbers. Copper 8-hydroxy quinolinolate, a known fungicide for many synthetic rubbers, is also an effective accelerator for sulphur-cured EPD rubbers (Section IV, E). Where fast-curing light-colored stocks are required, cadmium diethyl dithiocarbamate may be used. A cure time of 10 minutes at 160°C is sufficient in many cases to give vulcanizates with acceptable physical properties. Zinc dimethyl or diethyl dithiocarbamate also gives fast-curing systems with variable bloom characteristics that need to be investigated for each specific compound.

3. Peroxide systems

In sulphur-cured EPD rubbers, the number of double bonds available limits the degree of crosslinking. Peroxide curing agents, however, can react with any of the tertiary hydrogens on the propylene groups to give vulcanizates with a greater number of crosslinks. Peroxide-cured EPD rubbers give light-colored vulcanizates with excellent resistance to heat aging and compression set. McGarvey and Veroeven[5] and Sieron[27] have shown that peroxide-cured compounds may be used at temperatures of up to 200°C.

In ethylene-propylene copolymer (EP) rubbers, unsaturated coagents can be used with organic peroxides to improve crosslinking efficiency[28]. Howarth, Cornell, and Olsen[24] have shown that similar improvements can apply to peroxides used to cure EPD rubbers. Although sulphur is an effective coagent for carbon black reinforced EP rubber, it is not effective in silica-reinforced EP or EPD rubbers. Similarly, DPMTT (1 phr), alone or in combination with triallyl cyanurate (1 phr), does not markedly improve the crosslinking efficiency of dicumyl peroxide.

Unsaturated crosslinking coagents, such as ethylene glycol dimethacrylate or trimethylolpropane trimethacrylate (TMPTM), are effective coagents for dicumyl peroxide. Details of rubbers crosslinked with sulphur and also with peroxides are given in Table III.

Although hot milling (Section IV, B) is very effective in improving the properties of sulphur-cured EPD rubbers (Table III, compounds 5, 7), it is less effective in rubbers cured with peroxides (compounds 6, 8). Hot milling Nordel 1040 rubber in the absence of p-quinone dioxime, followed by crosslinking with dicumyl peroxide and TMPTM, gives vulcanizates with inferior physical properties. Similar cold-milled rubbers have a very slow rate of cure. Activators as well as coagents for the peroxides are required for use with silica-reinforced EPD rubbers. Tetraethylthiuram disulphide (TETD) is effective in Enjay 3509, and p-quinone dioxime in Nordel 1040.

TABLE III

PROPERTIES OF SULPHUR- AND PEROXIDE-CURED EPD RUBBERS

Compound*	5	6	7	8	9**	10**
EPD rubber	Enjay 3509	Enjay 3509	Enjay 3509	Enjay 3509	Nordel 1040	Nordel 1040
Time of hot milling	Nil	Nil	10'/121°C	10'/121°C	Nil	10'/160°C
Curing system	Sulphur	Peroxide	Sulphur	Peroxide	Peroxide	Peroxide
p-Quinone dioxime, phr	-	-	-	-	1.0	1.0
Tetraethylthiuram disulphide, TETD, phr	1.0	1.0	1.0	1.0	-	-
Mooney properties at 138°C:						
time to scorch, min (5 pts rise)	7.0	7.3	9.0	8.5	8.5	4.0
Minimum viscosity, points	116	115	88	80	82	66
Cure index, Δ 30, min	1.4	4.6	2.5	3.2	5.4	1.4
Mooney viscosity, ML(1/4), 121°C	118	119	97	93	88	70
Tensile strength, psi	2600	2550	3400	2300	2200	1900
Ultimate elongation, %	650	570	570	520	580	580
Stress at 300% elongation, psi	600	850	1200	1100	900	800
Hardness, Shore "A"	72	70	68	64	68	60
Abrasive index, NBS	123	204	179	348	173	1000/
Compression set, %, after						
24 hr at room temperature	13.6	11.7	11.8	8.9	9.6	11.8
24 hr at 100°C	76.6	22.8	68.3	18.2	27.3	28.7
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	100	200	60	125	125	40

*Formulation: EPD rubber as shown, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; Hi-Sil 233, 50; polyethylene glycol, 1; stearic acid, 1. p-Quinone dioxime and TETD as shown. Compounds hot milled as shown.
Curing systems: sulphur system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5
peroxide system: dicumyl peroxide (40%), 9.0; trimethylolpropane trimethacrylate, 3.0.
All compounds cured 20 minutes at 160°C.

**Compare to compound 3, Table II.

As shown in Table III, peroxide-cured EPD rubbers have a greater resistance to compression set at elevated temperatures than similar rubbers cured with sulphur. Hot- or cold-milled peroxide-cured compounds based on Enjay 3509 are suitable for use in white or light-colored stocks (compounds 6,8), while similar compounds based on Nordel 1040 are suitable for black or dark-colored stocks (compounds 9, 10), especially where maximum abrasion resistance is required.

B. Silica Reinforcement of EPD Rubbers

1. Hot milling with fine-particle-size silica

As non-crystallizing elastomers, unfilled vulcanizates of EPD rubber have very low tensile strength. Reinforcing silica fillers impart high strength to the rubbers but adequate dispersion of the silica and the rubber is necessary to obtain the maximum reinforcing effect. As with butyl rubber[14], the state of cure of silica-filled rubbers can be improved by hot milling the filler and oil with the base rubber at temperatures of up to 200°C and in the presence of a chemical promotor. The proper milling temperature is important as some degradation can occur with such fillers as hard clay when mixed at temperatures in excess of 130°C .

Silica fillers can readily be incorporated into EPD rubber by hot milling either on a heated open roll mill or in an internal mixer. As shown in Figures 1 and 2, hot milling of Nordel 1040 for 10 minutes at 160°C gives vulcanizates with good physical properties, although milling temperatures as high as 200°C may be used[22]. Hot milling results in a modification of the silica structure and improved wetting between the filler and the polymer. While, in general, tensile strength, modulus, and abrasive index are increased by hot milling, tear strength is reduced. With Enjay 3509, hot milling for 5 minutes at 160°C (or 10 minutes at 120°C) is sufficient to give vulcanizates with good physical properties (Table II, compounds 2 and 4).

Maximum benefit from hot milling was obtained when the reinforcing filler (Hi-Sil 233), lubricating agent (stearic acid), pigment (carbon black), silica activator (polyethylene glycol), and other additives (p-quinone dioxime and chlorosulphonated polyethylene) were all included in the hot milling cycle. The zinc oxide, sulphur, and accelerators were added later at normal mixing temperatures.

2. Effect of heat promotors

For maximum physical properties in silica-reinforced EPD rubbers, hot milling in the presence of a heat promotor is necessary Promotors such as p-quinone dioxime, N-Me-N4 dinitrosoaniline (33% active) (MDNA), and dibenzo-p-quinone dioxime are all very effective. These

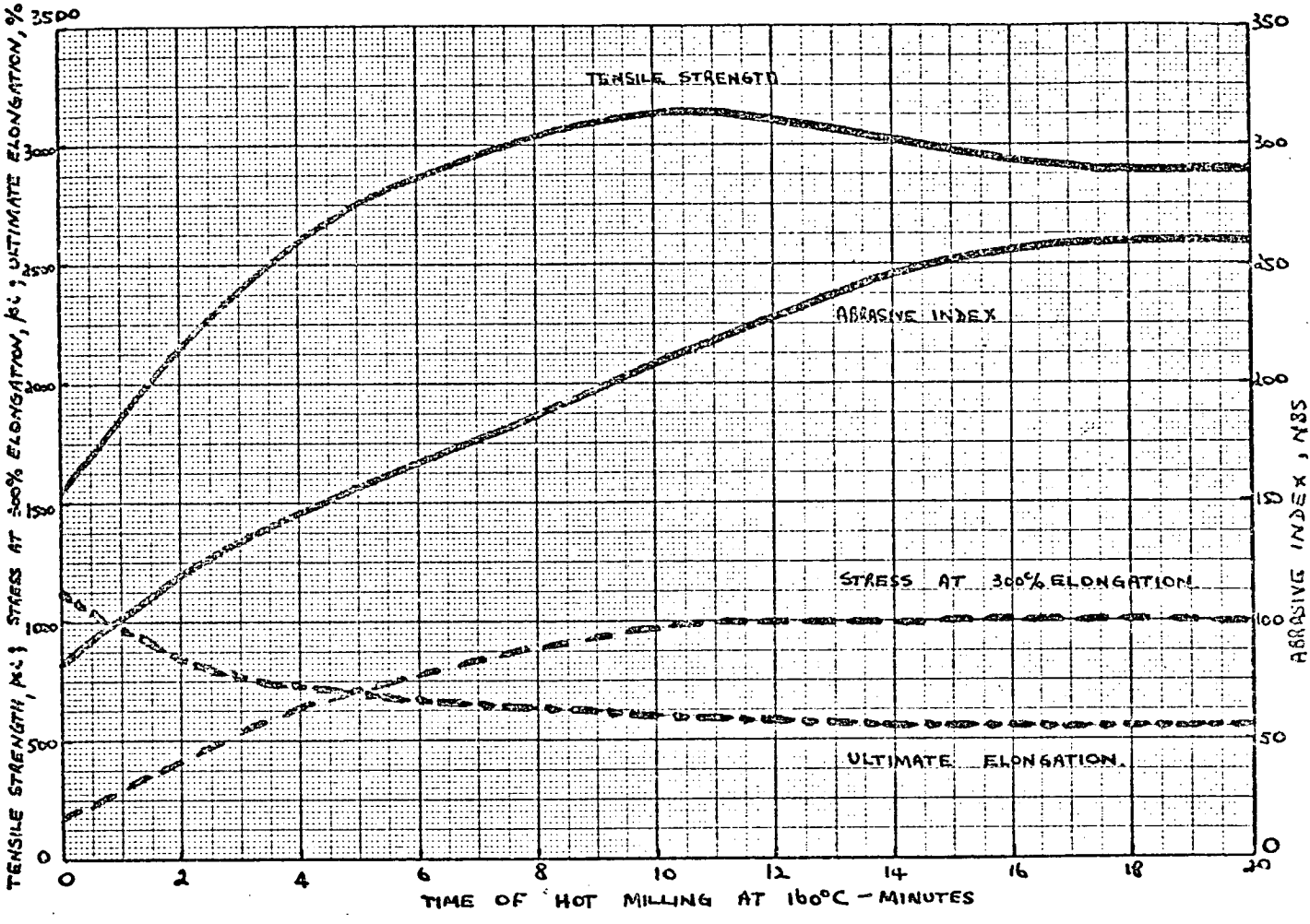

Figure 1. Effect of time of hot milling on the physical properties of silica-reinforced EPD rubber

Formulation: Nordel 1040, 100; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 50; polyethylene glycol, 1; p-quinone dioxime, 1; dioctyl sebacate, 20. Compounds hot-milled at 160°C for the times listed.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds were press cured for 20 minutes at 160°C.

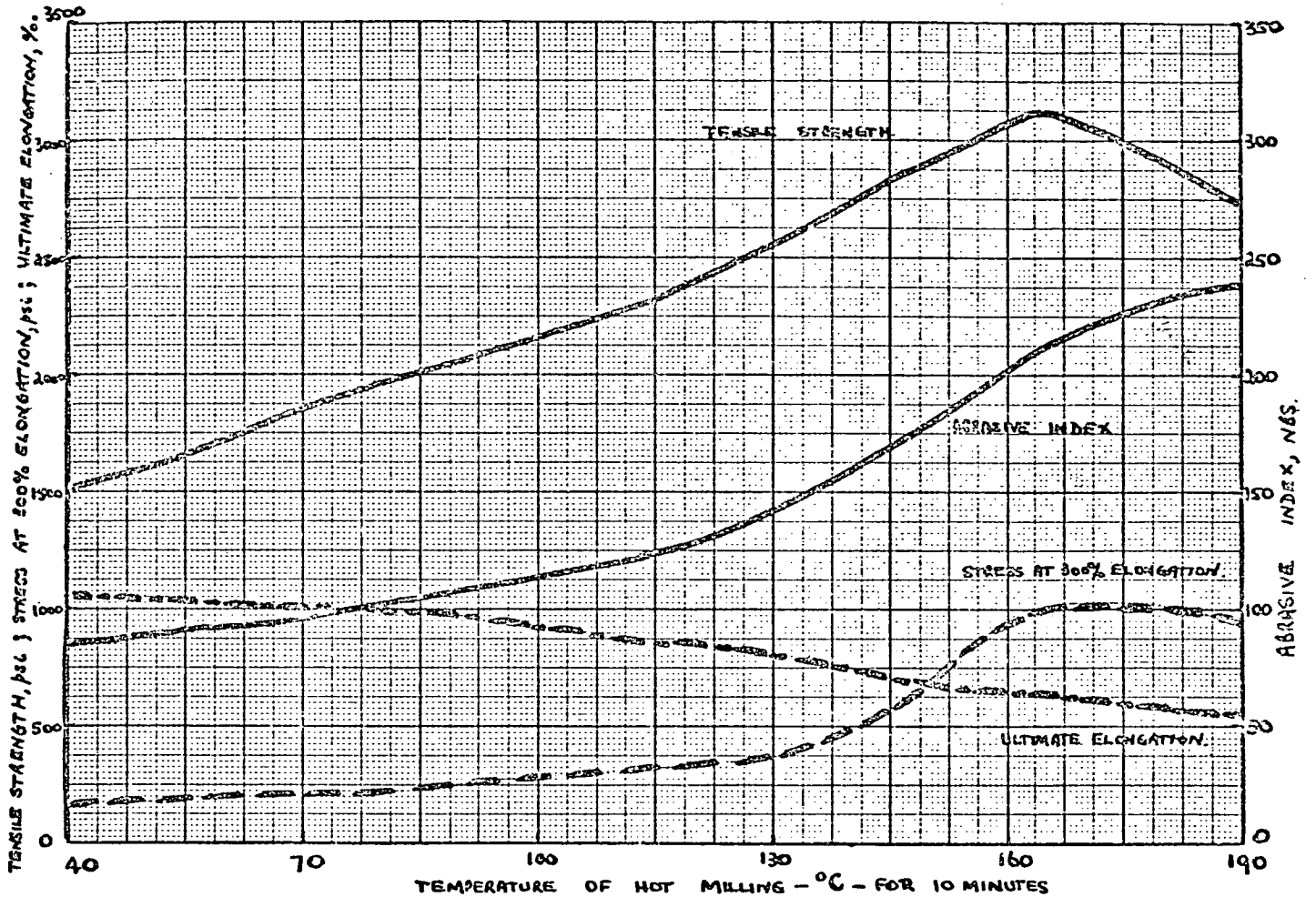

Figure 2. Effect of temperature of milling on the physical properties of silica-reinforced EPD rubber

Formulation: Nordel 1040, 100; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 50; polyethylene glycol, 1; p-quinone dioxime, 1; dioctyl sebacate, 20. Compounds hot-milled at the temperature listed for 10 minutes.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds were press cured for 20 minutes at 160°C.

promotors give brown colored stocks, hence their use should be restricted to black or dark colored vulcanizates. DPMTT, TETD, diphenyl guanidine (DPG), 4,4'-dithio-dimorpholine (DTDM), and hexamethoxymethyl melamine (HMMM) are also effective and are non-discoloring heat promotors.

As shown in Figure 3, p-quinone dioxime used at the 1 phr level is an efficient chemical promotor for hot-milled EPD rubbers plasticized with dioctyl sebacate. Higher levels of p-quinone dioxime seriously retard the curing system and give vulcanizates with inferior properties. However, the use of variable amounts of this heat promotor provides a convenient and easy way of adjusting the rubber viscosity and modulus of silica-reinforced compounds to almost any desired level. p-Quinone dioxime is also an efficient chemical promotor for silica-reinforced EPD rubbers plasticized with naphthenic oils.

The efficiency of several chemical promotors in hot- and cold-milled EPD rubbers is shown in Table IV. In the cold-milled Nordel 1040 EPD rubber, p-quinone dioxime seriously retards the cure. DPMTT, MDNA, DPG, and HMMM do not show any marked effect in cold-milled compounds. TETD and DTDM, however, improve the rate of cure of cold-milled compounds and give light colored, bloom-free vulcanizates when used at the optimum concentration of 1 phr.

With hot-milled compounds, all the promotors listed in Table IV are effective in improving the rate of cure and give vulcanizates with good physical properties. Hot-milled compounds show lower Mooney viscosities and better flow properties than cold-milled compounds. For black or dark colored rubbers, hot milling with p-quinone dioxime (1 phr) is suitable, while for white or light colored rubbers, hot milling in the presence of TETD (1 phr) or DTDM (1 phr) is recommended. As shown in Figures 1 and 2, the optimum time of hot milling was 10 minutes at 160°C.

3. Plasticizers for EPD rubbers

Generally, petroleum oil plasticizers, which are highly compatible with EPD rubbers, can be added in large quantities with only a moderate reduction in the physical properties of the rubber. The processing oils should be saturated, if possible, otherwise the double bonds present will scavenge the sulphur used in the vulcanization. White[30] and others[31] discuss the basic rules for selecting suitable plasticizers and extenders for EPD rubber and show that the physical properties of the vulcanizates will vary with the type and viscosity of the compounding oils.

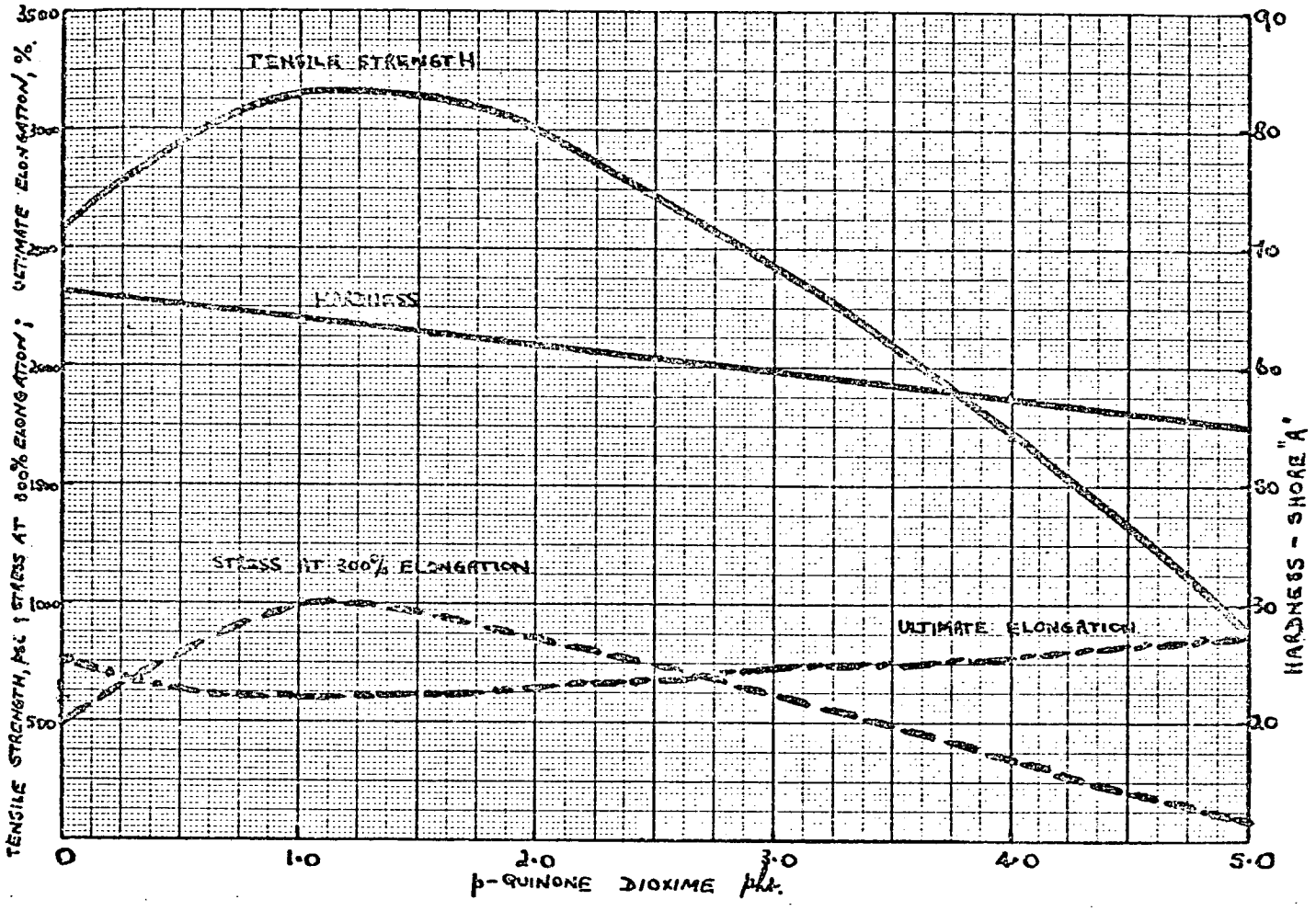

Figure 3. Effect of p-quinone dioxime concentrations on the physical properties of silica-reinforced EPD rubber

Formulation: Nordel 1040, 100; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 50; polyethylene glycol, 1; dioctyl sebacate, 20; p-quinone dioxime, as listed. Compounds hot-milled for 10 minutes at 160°C.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds press cured 20 minutes at 160°C.

TABLE IV

EFFECT OF ORGANIC PROMOTORS ON HOT- AND COLD-MILLED EPD RUBBERS

	Compound*	11	3	12	13	14	15
	Promotor**	Nil	p-Quinone dioxime	DPMTT	MDNA	TETD	HMMM
	Concentration, phr	-	1.0	1.0	3.0	1.0	2.0
Compounds cold milled	Mooney properties at 138°C: Time to scorch, min, (5 pts rise)	7.8	13.1	7.8	9.4	7.4	9.5
	Minimum viscosity, points	80	76	79	74	72	75
	Cure index, Δ30, min	2.2	34.5	1.7	3.2	1.4	2.0
	Tensile strength, psi	2900	1000	3250	2500	3050	2500
	Ultimate elongation, %	870	1000+	750	950	680	800
	Stress at 300% elongation, psi	325	100	270	350	600	400
	Hardness, Shore "A"	68	68	68	65	67	68
Compounds hot milled 10 min at 160°C	Mooney properties at 138°C: Time to scorch, min, (5 pts rise)	11.3	11.3	9.5	10.7	9.8	12.9
	Minimum viscosity, points	50	62	60	54	52	54
	Cure index, Δ30, min	4.1	4.2	3.1	3.8	3.0	4.6
	Tensile strength, psi	3100	3400	3280	3380	3200	2800
	Ultimate elongation, %	700	540	640	600	630	600
	Stress at 300% elongation, psi	500	1200	750	1000	830	850
	Hardness, Shore "A"	60	60	60	56	59	64

*Formulations: Nordel 1040, 80; Royalene X400, 40; Hi-Sil 233, 50; polyethylene glycol, 1; stearic acid, 1; chlorosulphonated polyethylene, 7.5. Promotor and hot and cold milling as listed.
Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. All compounds press cured 20 minutes at 160°C.

**DPMTT, dipentamethylenethiuram tetrasulphide
MDNA, N-Me-N4 dinitrosoaniline (33% active)
TETD, tetraethylthiuram disulphide
HMMM, hexamethoxymethyl melamine

Recently, oil-extended EPD rubbers have been introduced (Table I) and Whitehouse, Barnhart, and Michell[32], also Luh[33], have discussed the properties of these new rubbers. Royalene X400, an EPD rubber extended with 100 phr of naphthenic oil, is a convenient plasticizer for silica-reinforced EPD vulcanizates, and dioctyl sebacate has been used as a general purpose plasticizer as well. Oil-extended EPD rubber may also be used to improve the ozone resistance of silica-reinforced styrene-butadiene rubbers (Section IV, C,4).

Silica-reinforced EPD rubbers (for example, compound 3) with naphthenic or paraffinic oils, di-2-ethyl sebacate, adipate, azelate, phthalate, or polyether plasticizers, give vulcanizates with similar properties. The tri-2-ethylhexyl phosphate plasticizer slightly retards the curing system but is preferred, along with di-2-ethylhexyl sebacate, when flexibility at low temperatures is important (Section IV, D). The tricresyl phosphate plasticizer is not compatible with EPD rubber and methylated tall oil ester plasticizers seriously retard the curing system. Since silica-reinforced EPD rubbers need to be hot milled to develop maximum physical properties, low-volatility plasticizers should be used. General purpose EPD rubber compounds, hot-milled for 10 minutes at 160°C, show a loss in weight of about 2.0 percent.

4. Effect of silica activators and stearic acid

In order to develop an adequate rate of cure in silica-reinforced rubbers, it is necessary to use a glycol or similar type of polyhydric compound[8,9,14]. When water (or a volatile glycol) is driven off at high processing temperatures, undercures are likely to occur[34]. Recently, however, Bartrug[35] has stated that special activators, such as diethylene glycol, are to be avoided in silica-reinforced EPD rubbers if maximum reinforcement is to be obtained, as they interfere with the filler-polymer interaction.

Examination of a series of silica activators, such as diethylene glycol, polyethylene glycol, pentaerythritol 200, triethanolamine, and bis (hydroxymethyl) 1,4-cyclohexane, has shown that these compounds are all effective in improving the properties of silica-reinforced EPD rubbers. The results given for compound 3 in Table IV are typical. Generally, silica activators are added at the level of 6 percent of the silica loading[8,9]. However, optimum physical properties are obtained at an activator level of about 2 percent of the silica loading (1 phr of activator per 50 phr of Hi-Sil 233). Higher levels of silica activators result in a reduction of physical properties. Polyethylene glycol and bis (hydroxymethyl) 1,4-cyclohexane are effective in silica-reinforced EPD rubbers plasticized with either naphthenic oils or ester-type plasticizers. Activators based on polyalkanolpolyamines generally retard curing systems based on zinc oxide, sulphur, TMTD, DPMTT, and MBT.

The presence of stearic acid is not essential for good vulcanization but small amounts (1 phr) improve processability and dispersion of the fillers, especially at high loadings. In the absence of stearic acid, there is no marked improvement in the physical properties of the EPD rubber vulcanizates.

5. Use of special additives

The rate of cure of mineral-filled EPD rubbers can be improved by the addition of polar rubbers such as chlorosulphonated polyethylene[22,36], or of other chlorine-containing compounds. Improvements are obtained in the scorch rate, compression set, permanent set, and stress at 300 percent elongation. The addition of chlorosulphonated polyethylene also gives vulcanizates with the maximum heat resistance, especially when used in conjunction with antimony trioxide[27] and high levels of zinc oxide[26]. In addition to covulcanizing with the EPD rubber, chlorosulphonated polyethylene is believed to give a large increase in the modulus due to reaction between the chlorine and chlorosulphonyl groups and the active groups on the surface of the silica filler.

The addition of chlorosulphonated polyethylene (7.5 phr) or octachlorocyclopentene (1.5 phr) to hot-milled silica-reinforced EPD rubber plasticized with either dioctyl sebacate or a naphthenic oil gives the maximum improvement in general physical properties. Chlorine-containing compounds, such as polychloroprene (7.5 phr), polyepichlorohydrin (7.5 phr), nitrile-polyvinylchloride resin blend (7.5 phr), p-toluene sulphonyl chloride (2.0 phr), hexachloroethane (2.0 phr), and dichlorodiphenyl-trichloroethane (2.0 phr), are not effective in improving the cure rate of silica-reinforced EPD rubbers. Perchloropentacyclodecane (7.5 phr), a known flame-proofing agent for ethylene-propylene copolymer rubber (EPR)[37], also has no effect on the cure rate.

Both chlorinated paraffin wax (7.5 phr) and tetrachloro-p-benzoquinone (2.0 phr) improve the rate of cure of silica-reinforced EPD rubbers but are not as effective as chlorosulphonated polyethylene or octachlorocyclopentene. These chlorine-containing additives are effective with both Nordel 1040 and Enjay 3509 EPD rubbers and give the maximum improvement in physical properties when used with hot-milled silica-reinforced compounds. The additives have no effect on the processing characteristics of EPD compounds, but both chlorosulphonated polyethylene and octachlorocyclopentene give improvements in the compression-set resistance of EPD rubbers at room temperature and at 100°C.

In the absence of a chemical promotor such as p-quinone dioxime, chlorosulphonated polyethylene (7.5 phr) or octachlorocyclopentane (1.5 phr) improves the physical properties of EPD rubbers and can be used for the

production of white and light colored stocks. The combined use of these two chlorine-containing compounds in hot- or cold-milled EPD rubbers, as compared to their use individually, does not result in any improvement in physical properties. When rubbers with non-corrosive and non-staining properties towards metals are required, chlorine-containing additives should not be used.

Chemical analysis (C,H,N,Cl) of EPD rubbers, hot milled in the presence of p-quinone dioxime (1 phr) and octachlorocyclopentene (1 phr), alone and together, followed by purification by precipitation with methanol from a toluene solution (5% w/v), indicated that there was no chemical bonding between the additives and the polymer as a result of the hot milling process.

Recently Wolfe and Albin[38] have described the use of polyisocyanates as curing adjuvants for EPD rubbers. Compounds such as polymethylpolyphenylisocyanate (PMPPI) are effective in improving the cure rate, ultimate elongation, modulus, and compression-set characteristics of silica-reinforced EPD rubbers. The improvements in vulcanizate properties are believed to be due to a more effective reinforcement of the polymer by the filler. PMPPI added with the curing agents at the 3 phr level is very effective in improving the properties of hot-milled, silica-reinforced compounds activated with p-quinone dioxime (Table V, compound 16). Cure times of 10 minutes at 160°C give vulcanizates with good general physical properties.

In the absence of p-quinone dioxime, PMPPI is also effective for use with light colored stocks. The addition of PMPPI (3 phr) during the hot milling cycle does not result in any marked improvement in physical properties of the vulcanizates. For best results, the PMPPI is added, in the cold, along with the curing agents. As with most silica-reinforced rubbers, hot milling the rubber and the silica (compound 17) gives vulcanizates with superior physical properties to the cold-milled compound (compound 18). Details of vulcanizates containing PMPPI are given in Table V.

C. Physical Properties of EPD Rubbers

1. Silica-reinforced vulcanizates

Fine-particle-size silica fillers can be incorporated by up to 80 phr into EPD rubbers to give vulcanizates with good physical properties. At silica loadings above 60 phr, some retardation of the rate of cure can occur and longer cure times are necessary to obtain optimum properties in the vulcanizates.

Compounds plasticized with naphthenic oils, incorporated in the form of Royalene X400, have properties that are superior to those of vulcanizates containing the same amount of plasticizer incorporated in the form of a naphthenic light process oil. Figure 4 illustrates the physical properties obtained from a wide range of compounds containing hydrated silica filler and naphthenic

TABLE V

USE OF POLYMETHYLPOLYPHENYLISOCYANATE (PMPPI) IN EPD RUBBERS

Compound*	16	17	18
p-Quinone dioxime, phr	1	-	-
Time of hot milling at 160°C, min.	10	10	Nil
Mooney properties at 138°C:			
Time to scorch, min (5 pts rise)	12.9	10.2	12.6
Minimum viscosity, points	78	65	74
Cure index, Δ30, min	3.7	3.5	3.2
Mooney viscosity, ML(1+4), 121°C	80	98	70
Cured 10 min at 160°C			
Tensile strength, psi	2950	2600	2900
Ultimate elongation, %	540	650	840
Stress at 300% elongation, psi	1175	700	500
Hardness, Shore "A"	64	64	68
Cured 20 min at 160°C			
Tensile strength, psi	2900	3000	3200
Ultimate elongation, %	420	560	740
Stress at 300% elongation, psi	1700	1050	700
Hardness, Shore "A"	66	64	67
Abrasive index, NBS	269	247	167
Compression set, %, after			
24 hr at room temperature	8.6	11.3	10.7
24 hr at 100°C	63.5	69.8	74.6
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	200	100	50

*Formulations: Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; polyethylene glycol, 1; stearic acid, 1; Hi-Sil 233, 50. p-Quinone dioxime and hot milling as shown. PMPPI, 3, and curing agents added on a cold mill.

Curing System: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DMPTT, 0.75; MBT, 1.5

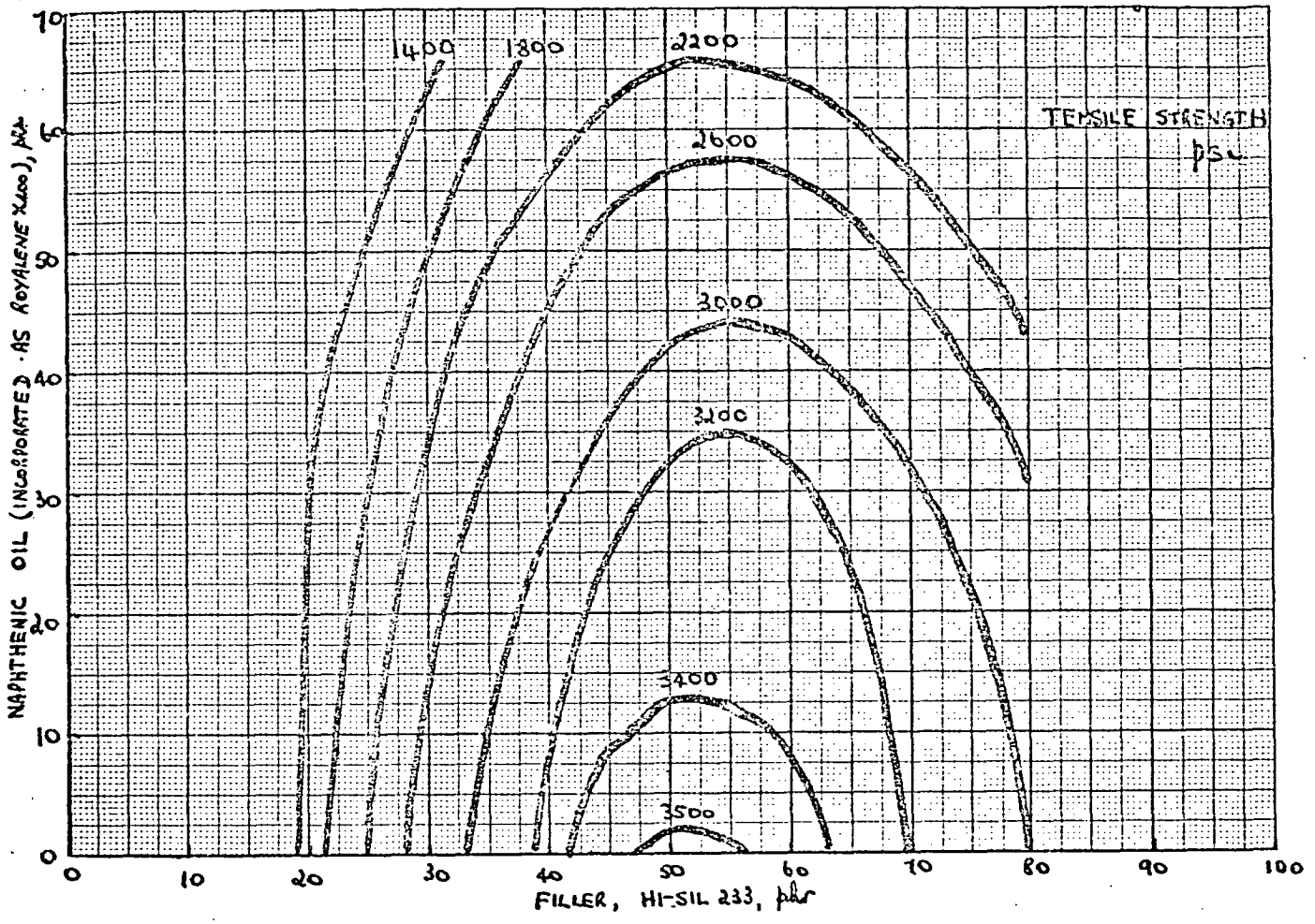

Figure 4a. Tensile strength, psi, of EPD rubbers at varying concentrations of silica and naphthenic oil.

Formulation: Nordel 1040, 100-W; Royalene X400, 2W (W is naphthenic oil loading as shown; chlorosulphonated polyethylene, 7.5; Hi-Sil 233 as shown; polyethylene glycol, 2% of the Hi-Sil 233 loading; HAF black, 3; stearic acid, 1; p-quinone dioxime, 1. Compounds hot milled for 10 minutes at 160°C.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds press cured for 20 minutes at 160°C.

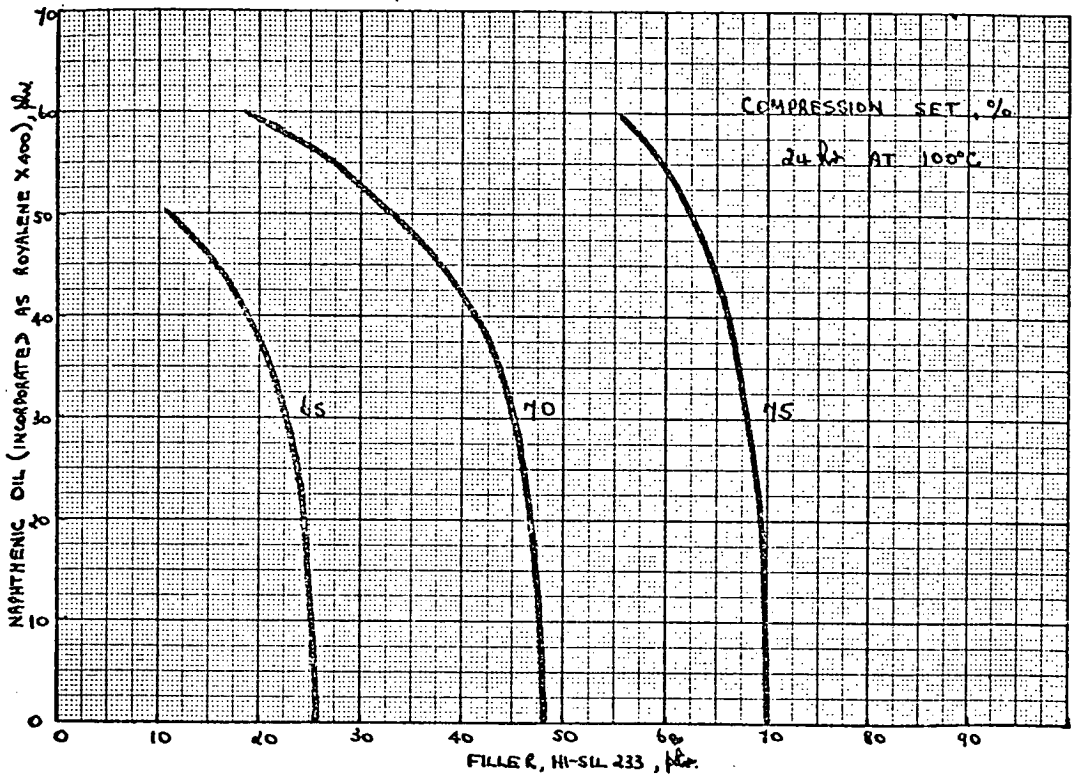

Figure 4b. Compression set, 24 hr at 100°C, %, of EPD rubbers at varying concentrations of silica and naphthenic oil

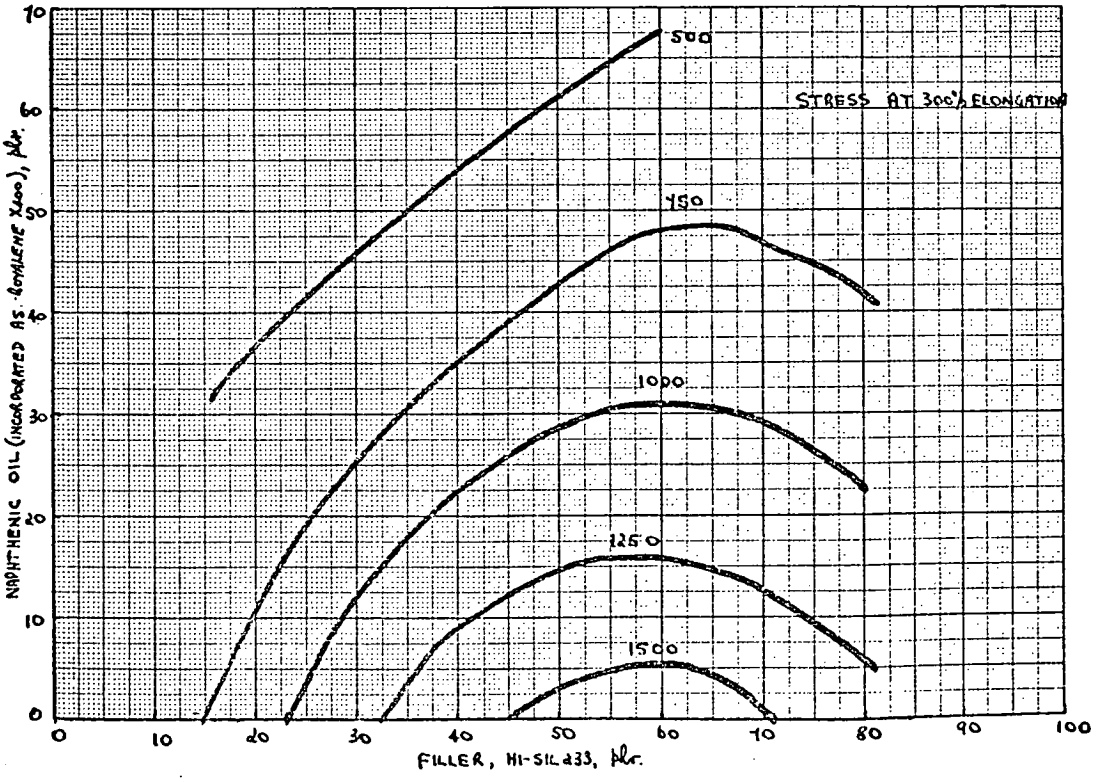

Figure 4c. Stress at 300% elongation of EPD rubbers at varying concentrations of silica and naphthenic oil

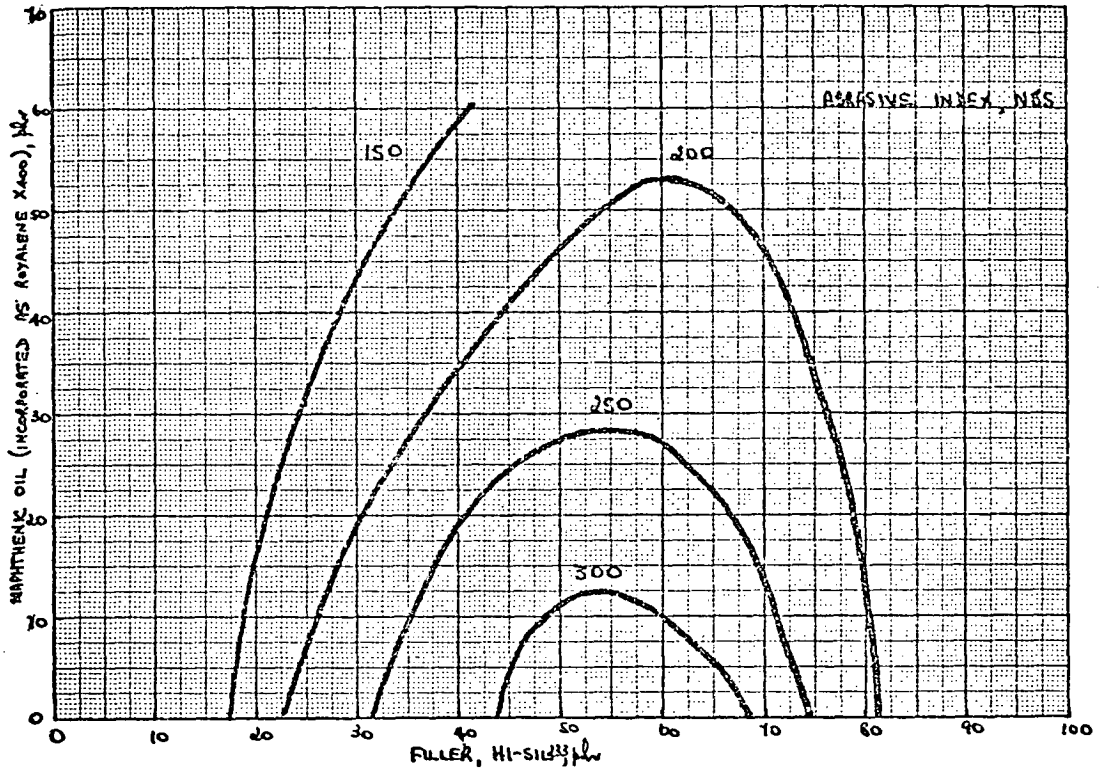

Figure 4d. Abrasive index, NBS, of EPD rubbers at varying concentrations of silica and naphthenic oil

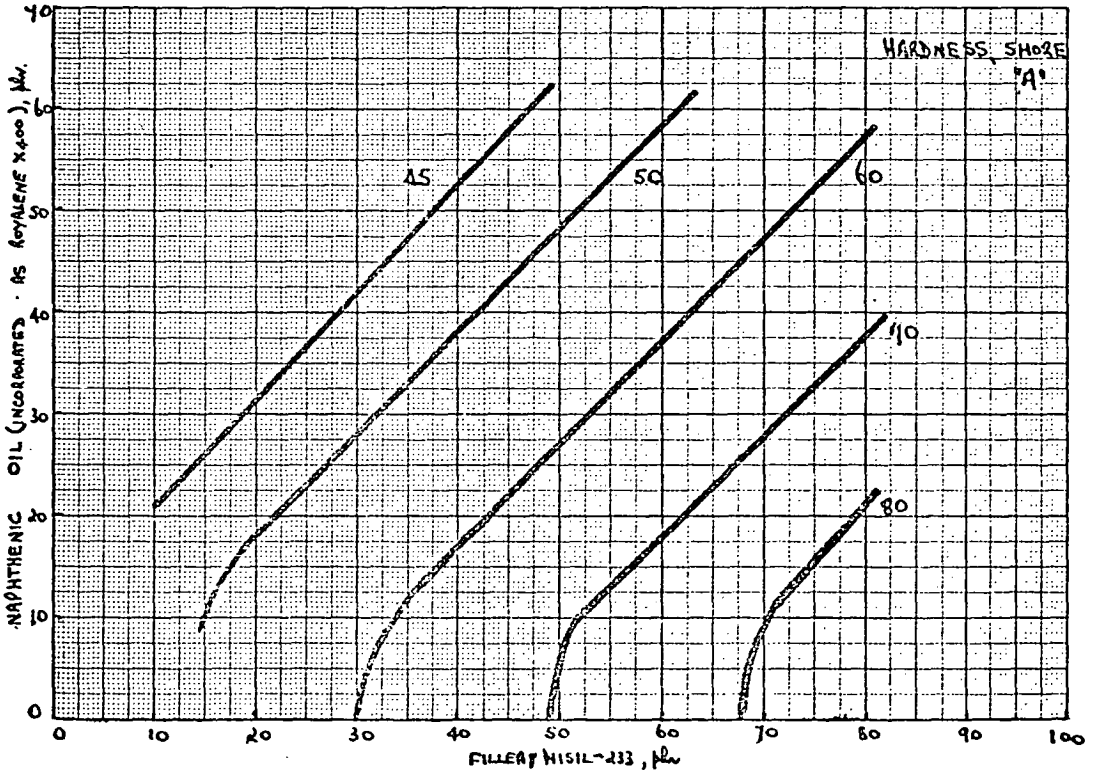

Figure 4e. Hardness, Shore A, of EPD rubbers at varying concentrations of silica and naphthenic oil

oil plasticizer. As shown in Figure 4a, the maximum tensile strength is obtained with a filler loading of about 50 phr of silica. A series of high quality compounds with a hardness range of from 45 to 71, Shore "A", can be obtained by varying the naphthenic oil plasticizer content from 0 to 60 phr in compounds containing a silica loading of 50 phr. The physical properties of such compounds are listed in Table VI.

All the vulcanizates have good tensile strength, elongation at break, modulus, and abrasion resistance. The compression-set properties are equal to those of silica-reinforced styrene-butadiene rubbers and stressed samples show excellent resistance to attack by ozone.

Dioctyl sebacate used as a low-temperature plasticizer for EPD rubbers (compound 1) gives vulcanizates with good general physical properties and with better processing characteristics and lower abrasion resistance than compounds plasticized with an equivalent amount of naphthenic oil.

2. Use of mixed fillers

To reduce compound costs, part of the silica filler may be replaced by other fillers with results as shown in Table VII. The replacement of half the silica (25 phr) by HAF black (compound 25), anhydrous silica (compound 31), or vinyl-coated silica does not markedly affect the vulcanizate properties.

Magnesium silicate (compound 26), calcium carbonate (compound 28), titanium dioxide (compound 29), antimony trioxide (compound 30), and hydrated aluminum silicate, in addition to 25 phr of silica, give vulcanizates with reduced physical properties.

Where compound cost is important, a filler combination of Hi-Sil 233 (25 phr) and kaolin hard clay (25 phr) (compound 27) gives vulcanizates with good general physical properties and an abrasion resistance adequate for many applications.

3. Carbon black reinforced vulcanizates

In order to compare the reinforcing action of fine-particle-size silica (particle diameter, Hi-Sil 233, 22 mμ[14]) with a similar-particle-size carbon black (particle diameter, HAF black, 29 mμ[14]), vulcanizates were prepared and tested as detailed in Table VIII.

Both hot- and cold-milled carbon black reinforced compounds were found to have better processing characteristics than silica-filled compounds at equivalent filler loadings. Sulphur-cured, carbon black reinforced

TABLE VI
PHYSICAL PROPERTIES OF EPD RUBBERS CONTAINING 50 PHR OF HI-SIL 233

Compound*	19	20	3	21	22	23	24
Nordel 1040 EPD rubber, phr	100	90	80	70	60	50	40
Royalene X400 EPD rubber, phr	0	20	40	60	80	100	120
Oil loading**, phr	0	10	20	30	40	50	60
Tensile strength, psi	3500	3450	3300	3250	3000	2750	2500
Ultimate elongation, %	500	520	540	600	620	640	700
Stress at 300% elongation, psi	1600	1350	1200	900	700	630	575
Hardness, Shore "A"	71	68	62	57	53	49	45
Abrasive index, NBS	310	310	275	225	200	175	165
Compression set after 24 hr at 100°C, %	71	71	71	71	71	74	74
Volume swell after 24 hr in ASTM, fuel B, R.T., %	117	110	105	101	97	95	92
Specific gravity	1.124	1.113	1.103	1.095	1.087	1.080	1.074
Mooney viscosity, ML(1/4), 121°C	114	90	76	69	66	65	64
Cost, cents/lb	26.4	25.4	24.4	23.6	22.9	22.2	21.6

*Formulations: Nordel 1040, Royalene X400 and plasticizer, as listed; Hi-Sil 233, 50; polyethylene glycol 4000, 1; stearic acid, 1; HAF black, 3; p-quinone dioxime, 1; chlorosulphonated polyethylene, 7.5. Compounds hot milled 10 min at 160°C.
Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. All compounds press cured 20 minutes at 160°C.

**Incorporated as Royalene X400 an oil-extended EPD rubber containing 100 phr of naphthenic oil.

TABLE VII

EFFECT OF MIXED FILLERS ON EPD RUBBERS

Compound*	25	26	27	28	29	30	31
Added filler, 25 phr	HAF black	Magnesium silicate	Kaolin hard clay	Calcium carbonate	Titanium dioxide	Antimony trioxide	Anhydrous silica
Tensile strength, psi	3100	2900	3100	2000	2300	2700	3600
Ultimate elongation, %	460	560	570	500	550	700	700
Stress at 300% elongation, psi	1600	950	1200	650	650	475	800
Hardness, Shore "A"	57	55	55	53	50	48	62
Abrasive index, NBS	265	109	137	84	153	138	249
Compression set, %, after							
24 hr at room temperature	5.7	4.8	5.0	4.3	4.2	7.3	11.9
24 hr at 100°C	67.5	70.4	65.1	67.2	64.0	65.0	74.4

*Formulation: Nordel 1040, 80; Royalene 400, 40; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 25; polyethylene glycol, 0.5; stearic acid, 1. Added filler as listed, 25. Compounds hot milled 10 minutes at 160°C.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. In compound 28, an extra 0.5 phr of polyethylene glycol was added before the hot-milling cycle. All compounds cured 20 minutes at 160°C.

TABLE VIII

CARBON BLACK REINFORCED EPD RUBBERS

Compound*	32**	33**	34**	35**
p-Quinone dioxime, phr	1	-	1	-
Time of hot milling	10'/160°C	Nil	10'/160°C	Nil
Curing system	Sulphur	Sulphur	Peroxide	Peroxide
Mooney properties at 138°C:				
Time to scorch, min (5 pts rise)	8.2	7.0	4.1	5.7
Minimum viscosity, points	60	50	61	50
Cure index, Δ 30, min	3.2	2.5	1.3	1.4
Mooney viscosity, ML(1/4), 121°C	70	62	66	57
Tensile strength, psi	2900	2500	2100	2050
Ultimate elongation, %	370	460	400	480
Stress at 300% elongation, psi	2300	1400	1250	1050
Hardness, Shore "A"	60	70	58	62
Abrasive index, NBS	440	240	1000/	600/
Compression set, %, after				
24 hr at room temperature	5.3	14.2	13.3	12.7
24 hr at 100°C	66.2	60.2	14.8	18.6
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	500	450	175	75

*Formulation: Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; HAF black, 53; stearic acid, 1. p-Quinone dioxime and hot milling as listed.
Curing systems: sulphur type: zinc oxide 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5
peroxide type: dicumyl peroxide (40%), 9.0; trimethylolpropane trimethacrylate, 3.0
Compounds cured 20 minutes at 160°C.

**Equivalent silica-reinforced compounds: 32, Compound 3, hot milled
33, Compound 3, cold milled
34, Compound 10
35, Compound 9

compounds show good tensile strength, modulus, and abrasion resistance properties and poor cut-growth resistance. Their compression-set properties are similar to those of silica-reinforced compounds. Peroxide-cured carbon black reinforced compounds show superior physical properties as compared to sulphur-cured compounds and have excellent resistance to abrasion and compression set at elevated temperatures, and good cut-growth resistance. Cold-milled carbon black reinforced EPD rubbers have properties adequate for many applications, while hot milling improves certain properties but usually not to the same extent as it does for EPD rubbers reinforced with silica.

4. Blends of EPD rubbers with other elastomers

EPD rubbers are known to blend with other elastomers to give vulcanizates with improved ozone resistance. Sutton[39] has described the properties of some of these blends that are reinforced with carbon black. Oil-extended EPD rubber is very effective in improving the ozone resistance of silica-reinforced SBR compounds. For effective protection, the EPD rubber content should be at least 5 phr, and levels of 10 phr (20 phr for an oil-extended EPD rubber containing 100 phr of naphthenic oil) can be incorporated without markedly affecting the general physical properties of the vulcanizates.

Typical properties of SBR-EPD rubber blends are given in Table IX. Silica-reinforced SBR compounds cured with a conventional sulphur-accelerator system and with the zinc oxide level reduced to 1 phr have good physical properties and adequate resistance to heat aging at 70°C. As shown in Table IX, an antiozonant alone (3 phr, compound 37), or an EPD rubber alone (20 phr oil-extended compound 38), will not markedly improve the ozone resistance of an unprotected silica-reinforced SBR vulcanizate (compound 36).

The combined use of an antiozonant and an EPD rubber, however, gives vulcanizates (compound 39) with good physical properties and excellent ozone resistance. Carbon black reinforced SBR compounds may also be protected against ozone by this antiozonant-EPD rubber combination. The antiozonant N,N'-bis(1-methyl heptyl)-p-phenylenediamine (BMHPD, 3 phr), is very effective in silica-reinforced SBR compounds, although N,N'-bis(1,4 dimethyl pentyl)-p-phenylenediamine and N-isopropyl-N'-phenyl-p-phenylenediamine may also be used. The ozone resistance of the vulcanizates is not improved by the incorporation of sun-checking waxes (2 phr).

Silica-reinforced SBR-EPD rubber blends process easily and stearic acid lubricant is not required. Fast curing stocks are obtained by the use of triethanolamine activator (0.5 phr) with a resin softener (5 phr) to maintain the cut-growth resistance. Coumarone-indene resins, terpene-resin acid blends, and novolac-type and non-heat advancing phenolic resins are suitable. A typical vulcanizate with excellent ozone resistance is compound 40 (Table IX).

TABLE IX

BLENDS OF EPD RUBBER WITH SBR

Compound*	36	37	38	39**	40
Elastomers:					
Royalene X400***, phr	-	-	20	20	20
SBR 1502, phr	100	100	90	90	90
Light process oil, 10 phr	10	10	-	-	-
Antiozonant, 3 phr	-	BMHPD****	-	BMHPD	BMHPD
Mooney properties at 138°C:					
Time to scorch, min (5 pts rise)	11.1	9.3	9.5	8.7	7.3
Minimum viscosity, points	88	74	112	97	72
Cure index, Δ 30, min	4.1	2.1	3.3	2.6	1.6
Tensile strength, psi	2400	2500	2700	2700	2730
Ultimate elongation, %	600	650	570	620	670
Stress at 300% elongation, psi	800	670	900	800	700
Hardness, Shore "A"	63	63	66	65	66
Abrasive index, NBS	140	126	146	129	104
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	75	30	175	110	150
Ozone resistance, 50 pphm, 38°C	6				
Bent loop, time to crack, hr					
Unaged	6	12	6	1000+	1000+
Aged 70 hr at 70°C	6	6	6	1000+	1000+

*Formulation: Elastomer, process oil, antiozonant, as shown; Hi-Sil 233, 45; HAF black, 3; polymerized trimethyl dihydroquinoline, 1; zinc oxide, 1; benzothiazyl disulphide, 1.5; DOTG, 0.75; DPMTT, 0.5; sulphur, 3. In addition, compound 52 contains triethanolamine, 0.5; coumarone-indene resin (medium), 5. All compounds cured 15 minutes at 154°C.

**Compression set: 24 hr at room temperature, 6.3%; 24 hr at 100°C, 68.6%.

***An oil-extended EPD rubber containing 100 phr of naphthenic oil.

****N,N'-bis(1-methyl heptyl)-p-phenylene diamine.

Oil-extended EPD rubbers can also be blended with silica-reinforced blends of SBR and polybutadiene rubbers. Expanded vulcanizates of this type have excellent resistance to ozone and to abrasion.

D. Heat and Cold Resistance of EPD Rubbers

The saturated nature of the molecular backbone and the low concentration of pendant unsaturation enables general purpose EPD rubbers to be serviceable at 120°C, while special compounding permits long term service at 150°C [8,9,26]. Although carbon black reinforced compounds have superior heat resistance to mineral-filled compounds, the use of silica in EPD rubbers gives vulcanizates with a heat resistance adequate for many applications. Where maximum heat resistance is required, perioxide curing systems should be used.

Compounds processed by hot milling have superior physical properties and are less sensitive to heat aging than cold-milled compounds. Hot-milled compounds, heat aged at 100°C for 7 days, show a slight reduction in tensile strength and ultimate elongation and a hardness increase of several points. Heat aging for from 16 to 24 hours at 100°C is a convenient method of improving the modulus and compression-set characteristics of silica-reinforced EPD rubbers. The properties of cold-milled EPD rubbers can also be greatly improved after molding by an oven cure of up to 72 hours at 100°C.

For many military applications of rubber, flexibility at low temperatures is required. EPD rubbers do not crystallize at low temperatures and high quality compounds are reported[9] to remain flexible down to from -50°C to -60°C and to have brittleness temperatures as low as -70°C.

Tests carried out on hot-milled silica-reinforced EPD rubbers plasticized with 20 phr of di-2-ethyl hexyl sebacate indicate that the limit of low-temperature serviceability, as assessed by the Gehman T5 value, is about -58°C. Compounds containing naphthenic oil plasticizers or blends of these and di-2-ethyl hexyl sebacate are less flexible at low temperatures. The Gehman low-temperature values and the temperature of retraction values of two EPD rubbers are given in Table X. Compounds plasticized with tri-2-ethyl hexyl phosphate exhibit low-temperature properties similar to compounds plasticized with di-2-ethyl hexyl sebacate.

Recently, Wilson[40] has shown that hot-milled sulphur-cured EPD rubbers have better low-temperature flexibility than hot milled, peroxide-cured rubbers, and both are superior to cold-milled compounds. Vulcanizates reinforced with silica have low-temperature properties similar to compounds reinforced with HAF carbon black.

TABLE X

LOW TEMPERATURE PROPERTIES OF EPD RUBBERS

Compound	1*	3*
Plasticizer, phr	Dioctyl sebacate, 20	Naphthenic oil, 20
Gehman low temperature stiffness, °C.		
T_2	-46	-28
T_5	-58	-48
T_{10}	-62	-51
T_{100}	Below -65	-60
Low temperature retraction, °C		
TR10	-55	-46
TR30	-49	-39
TR50	-43	-33
TR70	-35	-26

*See Table II

E. Ozone, Chemical, Fungal, and Weather Resistance of EPD Rubbers

Properly compounded carbon black reinforced EPD rubbers have excellent ozone resistance[8,9,10]. Stressed silica-reinforced EPD rubber vulcanizates also show excellent ozone resistance and no signs of cracking after exposure at 38°C to an ozone concentration of 50 pphm for 1000 hours.

The vulcanizates have good resistance to such polar materials as water, phosphate esters, and glycols, as well as to many acids and

alkalies, but swell considerably in aliphatic and aromatic solvents, chlorinated hydrocarbons, and certain mineral oils. The volume-swell characteristics of a range of silica-reinforced vulcanizates are given in Table VI.

The U. S. Army has a continuing need for fungal-resistant rubbers to be used for molded components, footwear, coated fabrics, and is evaluating the effects of commonly used fungicides on various rubbers[41]. Black and non-black EPD rubbers, plasticized with naphthenic oils (20 phr) and crosslinked with accelerators based on tetramethylthiuram disulphide and 2-mercaptobenzothiazole, have excellent fungal resistance. Vulcanizates show no fungal growth after tests in the laboratory or after exposure in a tropical test chamber. Phosphate and phthalate ester plasticizers with good antifungal properties[42] may also be used in EPD rubbers.

Although copper 8-hydroxy quinolinolate will improve the cure rate of silica-reinforced EPD rubbers, its presence is not required to ensure adequate fungal resistance of the vulcanizates. EPD rubbers show good resistance to fungi during soil burial tests. Black and non-black vulcanizates exposed for eight weeks and tested at two weekly intervals show good retention of general physical properties. Water leaching of vulcanizates before soil burial does not markedly affect their physical properties or their fungal resistance. Details are given in Table XI.

EPD rubber vulcanizates, unless protected by a screening agent such as carbon black or titanium dioxide, are very sensitive to deterioration by ultraviolet light. As shown in Table XI (compounds 41,42), unprotected vulcanizates are seriously degraded after exposure to ultraviolet light for 100 hours, while vulcanizates containing carbon black, 3 phr, (compound 3) show good retention of physical properties.

In the absence of screening compounds, both Nordel 1040 and Enjay 3509 vulcanizates are seriously degraded by ultraviolet light. For adequate protection, they require carbon black or combinations of color pigments and titanium dioxide.

Properly compounded silica-reinforced EPD rubbers possess good weathering characteristics. As shown in Table XII, black, olive drab, and white compounds showed adequate retention of physical properties and no surface deterioration after outdoor exposure at Natick for 6 months. Red compounds (iron oxide pigment), 6 phr, and dark gray compounds (titanium dioxide and fine thermal black, 5:1), 6 phr, as well as vulcanizates heat aged for 16 hours at 100°C were also found to possess good weathering resistance.

TABLE XI

FUNGAL RESISTANCE OF EPD RUBBERS

Compound*	3	41	42
Elastomer, 80 phr	Nordel 1040	Enjay 3509	Enjay 3509
Fungicide, 0.5 phr	Nil	Nil	Cu8-hydroxy quinolinolate
Activator, 1 phr	p-Quinone dioxime	TETD	TETD
Carbon black, phr	3	-	-
Fungal resistance, ASTM1924-61T, 40 days exposure	No growth	No growth	No growth
Tropic chamber exposure, 30°C, 87-92% R.H., 90 days	No growth	No growth	No growth
Physical properties, as molded, unaged:			
Tensile strength, psi	3400	4000	2850
Ultimate elongation, %	560	620	520
Stress at 300% elongation, psi	1150	1100	1250
Hardness, Shore "A"	61	67	67
Physical properties, after soil burial for 8 weeks			
Tensile strength, psi	3200	3350	2900
Ultimate elongation, %	620	570	540
Stress at 300% elongation, psi	900	1000	1000
Hardness, Shore "A"	63	69	69
Physical properties, as molded, after 100-hr weatherometer exposure			
Tensile strength, psi	3100	1000	1350
Ultimate elongation, %	550	280	310
Stress at 300% elongation, psi	1200	-	1300
Hardness, Shore "A"	63	68	68
Physical properties after 100 hr weatherometer exposure and soil burial for 8 weeks			
Tensile strength, psi	2800	1000	1450
Ultimate elongation, %	600	300	350
Stress at 300% elongation, psi	900	1000	1100
Hardness, Shore "A"	63	69	69

*Formulations: Compound 3, see Table II. Compounds 41, 42: Enjay 3509, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; Hi-Sil 233, 50; polyethylene glycol, 1; stearic acid, 1; TETD, 1; zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Fungicide as listed. All ingredients milled on cold mill. Stock then hot milled 10 min at 121°C. All compounds cured 20 min at 160°C. Rubbers required for fungal testing were molded in a chrome-plated mold (6 x 6 x 0.075 inches) with no mold lubricant.

TABLE XII

WEATHER RESISTANCE OF EPD RUBBERS

Compound*	Color	Physical Properties	Period of outdoor exposure at Natick** Nil (as molded)	3 months	6 months
3	Black	Tensile strength, psi	3500	3500	3200
		Ultimate elongation, %	540	550	480
		Stress at 300% elongation, psi	1225	1300	1650
		Hardness, Shore "A"	59	61	66
43	Olive drab	Tensile strength, psi	3550	2900	2600
		Ultimate elongation, %	560	560	470
		Stress at 300% elongation, psi	1000	1000	1350
		Hardness, Shore "A"	59	61	63
44	White	Tensile strength, psi	3300	2350	2350
		Ultimate elongation, %	640	600	540
		Stress at 300% elongation, psi	575	600	800
		Hardness, Shore "A"	56	60	64

*Formulations: Compound 3, see Table II. Compound 43, same as compound 3 but with the HAF black (3 phr) replaced by olive drab pigment (8 phr) consisting of: chrome green, 85.5%; red iron oxide, 12.5%; fine thermal black, 2.0% by weight. Compound 44, Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; stearic acid, 1; polyethylene glycol, 1; Hi-Sil 233, 42. Compounds hot milled 10 min at 160°C.

Curing system and pigment: zinc oxide, 5; sulphur 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5; titanium dioxide, 14. All compounds cured 20 min at 160°C.

**Exposure commenced 1 October 1964.

F. Expanded Silica-Reinforced EPD Rubbers

Silica-reinforced EPD rubbers may be expanded with chemical blowing agents such as N,N-dinitrosopentamethylenetetramine (40%), azodicarbonamide, or p,p'-oxybis-(benzenesulphonylhydrazide), although the latter can cause some retardation of the curing system. The use of a surface-coated urea promotor with any of the blowing agents will eliminate unpleasant odors. To develop expanded rubbers with uniform cell structure, close control of the plasticity as determined by the silica and oil loading is required.

In silica-reinforced EPD rubbers, a press cure of 7 minutes at 160°C will give the required degree of expansion but the rubber in the cell walls will not have sufficient strength to prevent collapse of the cell network. A press cure of 15 minutes at 160°C, followed by an oven cure of 30 minutes at 160°C, gives expanded rubbers with good physical properties. Typical results for two expanded rubbers of differing densities are given in Table XIII.

Expanded silica-reinforced EPD rubbers have good tear, abrasion, compression-set, and dynamic-recovery properties. They also have good water resistance. Their oil resistance may be controlled, to some extent, by the plasticizer loading[43]. They can be made in a wide range of densities and colors using conventional processing equipment and techniques. Their ability to accept large amounts of compounding oils and their excellent ozone and weather resistance enables them to be blended with other elastomers such as butyl rubber to give products with excellent shock-absorbing properties[43]. Spenadel and coworkers[43,44], describe the use of expanded EPD rubber in automotive sponge applications and Machado[45] its use in shoe soling.

V. Military Potential of EPD Rubbers

For military use, general-purpose rubbers must have good resistance to heat aging, weathering, ozone, abrasion, compression set, and attack by chemicals and must be serviceable over the temperature range of from -50°C to +150°C. Suitably compounded EPD rubbers meet each of these requirements.

Either carbon black or silica-reinforced EPD rubbers should be suitable for such applications as tank track pads, gaskets and seals for ammunition boxes and other ordnance and electrical equipment, weather-stripping, miscellaneous vehicle components, and soling for military footwear. Their excellent electrical properties[46] could be used to advantage in the insulant and outer jacketing of military cables for arctic and tropical use. Their good low-temperature, heat, and abrasion properties suggest their use in heavy duty, off-the-road military tires[47].

TABLE XIII

EXPANDED SILICA-REINFORCED EPD RUBBERS

Compound*	45	46
N,N-dinitrosopentamethylenetetramine (40%)	5.0	7.5
Surface-coated urea promotor	1.5	2.25
Mooney properties at 138°C:		
Time to scorch, min (5 pts rise)	11.0	11.0
Minimum viscosity, points	44	44
Cure index, Δ 30, min	2.8	2.9
Mooney viscosity, ML(1+4), 121°C	64	67
Properties** of molded test sheet:		
Tear strength, pounds per inch	154	108
Tensile strength, psi	1200	950
Ultimate elongation, %	510	510
Stress at 300% elongation	450	350
Hardness, Shore "A"	55	45
Properties*** of a molded test slab:		
Density, lb/ft^3	27.7	17.8
Compression deflection, psi (25% deflection)	21.6	12.6
Compression set, % (24 hr at 70°C)	59.3	73.2
Water absorption, %	1.30	2.59
Recovery properties, sec****	1	1

*Formulation: Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 50; p-quinone dioxime, 1; polyethylene glycol, 1; stearic acid, 1. Compounds hot milled 10 min at 160°C.
Curing and blowing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5; blowing agent and blowing promotor as listed; petroleum jelly, 5. Compounds press-cured 15 min at 160°C, followed by an oven cure for 30 min at 160°C. In all cases, a mold loading of 85% nominal capacity was used.

**From a 6 x 6 x 0.75 inch mold.

***From a 3 x 3 x 0.50 inch mold.

****Ref 43. Rating: 1 sec or less, good;
1.5 sec or more, poor.

Their excellent resistance to polar liquids, phosphate ester-based plasticizers and fluids, and isopropyl nitrate propellants[48] indicates that they could be used for seals and gaskets that are in contact with these materials. These rubbers also have dynamic applications[49].

Synthetic fabrics coated with EPD rubber should be suitable for ponchos, foul weather clothing, heavy duty truck and gun covers, and inflated structures such as airhouses and liferafts. Expanded EPD rubbers, which are characterized by good shock-absorbing and thermal-insulating properties, should find applications in military packaging and in cold weather clothing and footwear.

VI. Conclusions

Hydrated silica is an effective, low-cost, non-black, reinforcing filler for the amorphous ethylene-propylene diene rubbers at present available in the United States. High quality vulcanizates can be produced in all colors by suitable compounding. To obtain optimum vulcanizate properties it is necessary to hot mill the rubber and the silica in the presence of chemical promotors and silica activators. The rubbers may be crosslinked with either peroxide or sulphur curing systems.

Properly compounded silica-reinforced EPD rubber vulcanizates are usable over a temperature range of from -50°C to +150°C and have excellent resistance to ozone, heat aging, weathering, and fungal and chemical attack. They are not oil-resistant. Expanded silica-reinforced EPD rubbers with good physical properties can be produced by conventional processing techniques.

VII. Recommendations

The attractive properties of carbon black or silica-reinforced EPD rubbers warrant their investigation for many of the military applications described in Section V. Typical high quality vulcanizates should be examined to determine the applicability to them of the latest military standard on vulcanized rubber[50].

Because compounding has a marked effect on the weather resistance of EPD rubbers, there should be further outdoor exposures of black and non-black vulcanizates under temperate, desert, and tropical environments. The low-temperature properties of these rubbers should also be further studied by means of the new low-temperature testing techniques being developed by Wilson[40]. In addition, studies should be conducted on heat-curable and pressure-sensitive adhesives for EPD rubbers.

VIII. Acknowledgments

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IX. References

1. McCabe, R.F., Rubber Age, 96, 397 (1964)

2. U.S. Army Materiel Command, Contract No. DA19-129-QM-1944. Aldan Rubber Co., Philadelphia, Pa. (1961)

3. Anderson, H.H. and K.A. Eltzroth, Final Report, U.S. Army Materiel Command, Contract No. DA30-070-CML-916. General Tire and Rubber Co., Wabash, Ind. (1964)

4. Brueksch, W. and E. Hahn, Final Report, U.S. Army Materiel Command, Contract No. DA18-108-AMC-268A, U.S. Rubber Co., Wayne, N.J. (1964)

5. McGarvey, J.W. and W.M. Veroeven, Technical Report 64-2678, U.S. Army Materiel Command, Rock Island Arsenal, Rock Island, Ill., (1964)

6. Wilson, A., Rubber Technology Section Report No. 1, U.S. Army Natick Laboratories, Natick, Mass. (1964)

7. Schoenbeck, M.A., Rubber Chem. and Technol., 35, 1142 (1962)

8. Anon. "Enjay EPT/Ethylene Propylene Terpolymer." Enjay Chemical Co., Linden, N.J. (1964)

9. Anon. "Nordel Hydrocarbon Rubber." Technical Report, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. (1964)

10. Anon. "Royalene - the Crackless Rubber." Technical Bulletins, U.S. Rubber Co., Wayne, N.J. (1964)

11. Dudek, T.J. and F. Bueche, Rubber Chem. and Technol., 37, 894 (1964)

12. Anon. "The Behavior of ITAL-W4 in EPT Elastomer." Technical Service Report No. 431, International Talc Co., New York, N.Y. (1964)

13. Anon. "Mistron Vapor Reinforcement of Ethylene-Propylene Terpolymers." Rubber Technical Bulletins Nos. 45-50, Sierra Talc Co., South Pasadena, Calif. (1962-1964)

14. Bachmann, J.H., J.W. Sellers, M.P. Wagner, and R.F. Wolf, Rubber Chem. and Technol., 32, 1286 (1959)

15. Anon. "Hi-Sil 233 and Hi-Sil 215." Hi-Sil Bulletin No. 4, Pittsburg Plate Glass Co., Pittsburgh, Pa. (1963)

16. Anon. "Hi-Sil 215." Hi-Sil Bulletin No. 26. Pittsburgh Plate Glass Co., Pittsburgh, Pa. (1963)

17. Bartrug, N.G. and R.R. Meltz, "Hi-Sil 233 in Ethylene-Propylene Rubber" Hi-Sil Bulletin No. 25, Pittsburgh Plate Glass Co., Pittsburgh, Pa. (1963)

18. "Compounding Ingredients for Rubber," Third Edition, Rubber World, New York, N.Y. (1961)

19. Natta, G., G. Mazzanti, G. Crespi, A. Valvassori and G. Sartori, Rubber Chem. and Technol, 36,988 (1963)

20. Waddell, H.H., R.S. Auda, and J.V. Fusco, Rubber Age, 94, 427 (1963)

21. Auda, R.S. and J.R. Hooten, "Influence of Vulcanization Systems on the Performance of Ethylene-Propylene Terpolymers." Paper presented at meeting of the A.C.S. Division of Rubber Chemistry, Detroit, Mich. (1964)

22. Roche, I.D., Rubber Age, 93, 921 (1963)

23. Alliger, G. and I.J. Sjothun, "Vulcanization of Elastomers." Reinhold Publishing Corp., New York, N.Y. (1963)

24. Howarth, J.T., J.A. Cornell, and L.R. Olsen, Rubber World, 148, 5, 69 (1963)

25. Anon., Chem. and Eng. News., 41, No. 50,50 (1963)

26. Schoenbeck, M.A., "Nordel Hydrocarbon Rubber." Bulletin No. 1, E.I. du Pont de Nemours and Co., Inc., Wilmington, Del. (1964)

27. Sieron, J.K., Rubber World, 149, 58 (1963)

28. Lenas, L.P., Rubber Chem. and Technol, 37, 229 (1964)

29. Haxo, H., W. Bingham, and W. Whitehouse, Rubber Age, 255, (1963)

30. White, R.M., Rubber Age, 94, 897 (1964)

31. Anon, Rubber World, 149, 54 (1964)

32. Whitehouse, W.G., R.R. Barnhart, and J.M. Mitchell, Rubber World, 150, 39 (1964)

33. Luh, D.R., "Nordel 1070 E." Nordel Hydrocarbon Rubber Bulletin No. 3, E.I. du Pont de Nemours and Co., Inc., Wilmington, Del., (1965)

34. Anon. "The Effect of Processing Temperatures on the Activation of Hi-Sil 233." Technical Bulletin, Pittsburgh Plate Glass Co., Pittsburgh, Pa. (May 1964)

35. Bartrug, N.G. "Hi-Sil 233 Reinforcement of Ethylene-Propylene-Diene Rubber." Hi-Sil Bulletin No. 29, Pittsburgh Plate Glass Co., Pittsburgh, Pa. (1964)

36. Newman, N.F. "The Curing Behavior of Mineral-Filled EPD Rubber.", Report ELD-50896, Enjay Chemical Co., Linden, N.J. (1964)

37. Smith, W.C., "Enjay EPR Flame Retardant Compounds." Technical Information Sheet B-71, Enjay Chemical Co., Linden, N.J. (1962)

38. Wolfe, J.R. and J.R. Albin, Rubber Chem. and Technol., 37, 927 (1964)

39. Sutton, M.S., Rubber World, 149, 62 (1964)

40. Wilson, A., Private communication. U.S. Army Natick Laboratories, Natick, Mass. (1965)

41. Effect of Fungicides on Different Types of Rubber. Material Branch Report No. 4052-1, U.S. Army Engineering Research and Development Laboratories, Fort Belvoir, Va. (1963)

42. Berk, S., H. Ebert, and L. Teitell, Ind. Eng. Chem., 49, 1115 (1957)

43. Spenadel, L., Rubber World, 150, 69 (1964)

44. Cardillo, R.M. and L. Spenadel, Compounding and Properties of EPD Sponge. Paper presented at meeting of Southern Rubber Group, ACS Division of Rubber Chemistry, New Orleans, La. (1964)

45. Machado, J.J. Enjay EPD 3509 Closed-Cell Sponge for Shoe Soling. Report ELD-56311, Enjay Chemical Co., Linden, N.J. (1964)

46. Wolfe, J.R. and I.D. Roche, Rubber World, 149, 62 (1963)

47. Anon. Chem. and Eng. News, 43, No. 9, 16 (1965)

48. Liggins, T. Polyolefin Elastomers for Hydraulic System Fittings. Brit. Pat., 931,391 (1963)

49. Basenden, G.A., Compounding Ethylene-Propylene Terpolymers for Dynamic Applications. Paper presented at meeting of Division of Rubber Chemistry, ACS., Chicago, Ill. (1964)

50. MIL-STD-417(Ord), Rubber Compositions, Vulcanized, General Purpose, Solid. (1962)

APPENDIX I

Compounding Materials

Material	Trade Name	Supplier No.*
Anhydrous silica	Carb-O-Sil	3
Antimony trioxide	-	14
Azodicarbonamide	Celogen AZ	16
Benzothiazyl disulphide	Altax	32
Bis (hydroxymethyl) 1,4 cyclohexane	-	6
Calcium carbonate	Camel-WITE	9
Carbon black, fine thermal	P33 black	32
Carbon black, HAF	Philblack O	20
Chlorinated paraffin wax	Chlorowax 70	4
Chlorosulphonated polyethylene	Hypalon 40	5
Copper dimethyldithiocarbamate	Cumate	32
Copper-8-hydroxy quinolinolate	Milmer No. 1	18
Coumarone-indene resin (medium soft)	Neville R-15	17
Coumarone-indene resin (medium)	Cumar MH-1	1
Dibenzo-p-quinone dioxime	Dibenzo GMF	16
Dichlorodiphenyltrichloroethane	DDT	6
Dicumyl peroxide (40% active)	Dicup 40C	10
Di-2-ethylhexyl adipate	Flexol DOA	28
Di-2-ethylhexyl phthalate	Flexol DOP	28
Di-2-ethylhexyl sebacate	Flexol DOS	28
Di-orthotolylguanidine	DOTG	5

*See Appendix II

Material	Trade Name	Supplier No.*
Dipentamethylenethiuram tetrasulphide	DPMTT, Tetrone A	5
Diphenylguanidene	DPG	13
4,4'-Dithiodimorpholine	DTDM, Sulfasan R	13
Ethyleneglycol dimethacrylate	SR 206	22
Ethylene-propylene diene rubber (EPDR)	Nordel 1040	5
Ethylene-propylene diene rubber (EPDR)	Enjay 3509	7
Ethylene-propylene diene rubber, oil extended (EPDR)	Royalene X400	16
Hexachloroethane	-	6
Hexamethoxymethyl melamine	HMMM, Cymel 300	2
Hydrated aluminum silicate	Paragon clay	12
Hydrated silica	Hi-Sil 233	21
Kaolin hard clay	Dixie clay	32
Magnesium silicate	Mistron Vapor	24
2-Mercaptobenzothiazole	MBT, Captax	32
Methylated tall oil ester	Metalyn 100	10
Mixture of selected waxes	Sunproof Jr.	16
Naphthenic oil (light colored)	Light process oil	25
N,N'-bis (1,4 dimethylpentyl)-p-phenylenediamine	Eastozone 33	6
N,N'-bis (1-methylheptyl)-p-phenylene-diamine	UOP88	30
N,N-dinitrosopentamethylenetetramine (40% active)	Unicel ND	5
N-isopropyl-N'-phenyl-p-phenylenediamine	Flexzone 3-C	16

* See Appendix II

Material	Trade Name	Supplier No.*
N-Me-N4 dinitrosoanilene (33% active)	MDNA, Elastopar	13
Nitrile-polyvinylchloride resin blend	Paracril Ozo	16
Novolac-type phenolic resin	Schenectady SP8014	23
Octachlorocyclopentene	C58	11
p,p'-Oxybis-(benzenesulphonylhydrazide)	Celogen	16
Paraffinic oil plasticizer	Circosol 551	25
Pentaerythritol 200	"	10
Perchloropentacyclodecane	Declorane	11
Petroleum jelly	Pureline Petrolatum	19
Phenolic resin (non-heat advancing)	Bakelite CRR0909	28
Polyalkanolpolyamine	Nalco L-1718	15
Polychloroprene	Neoprene WRT	5
Polyepichlorohydrin	Hycar CHR	8
Polyether plasticizer	TP-110	26
Polyethylene glycol	Carbowax 4000	28
Polymerized trimethyl dihydroquinoline	Agerite Resin D	32
Polymethylpolyphenylisocyanate	PAPI	31
p-Quinone dioxime	GMF	16
SBR 1502	Philprene 1502	20
Selenium dimethyldithiocarbamate	Methyl Selenac	32
Surface-coated urea	BIK	16
Tellurium diethyldithiocarbamate	Ethyl Tellurac	32
Terpene-resin acid blend	Turgum S	12

*See Appendix II

Material	Trade Name	Supplier No.*
Tetrachloro-p-benzoquinone	Vulklor	16
Tetraethylthiuram disulphide	TETD, Thiuram E	5
Tetramethylthiuram disulphide	TMTD, Methyl Tuads	32
Titanium dioxide	Titanox RA40	27
p-Toluene sulphonyl chloride	-	6
Triallyl cyanurate	TAC	2
Tri (2-ethylhexyl) phosphate	Flexol TOF	28
Trimethylolpropane trimethacrylate	SR350	22
Vinyl coated silica	Santocel C (vinyl coated)	29
Zinc dimethyldithiocarbamate	ZDC, Methazate	16

*See Appendix II

APPENDIX II

Material Suppliers

No.

1. Allied Chemical Corp., Philadelphia, Pa.
2. American Cyanamid Co., Bound Brook, N.J.
3. Cabot Corp., Boston, Mass.
4. Diamond Alkali Co., Cleveland, O.
5. E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.
6. Eastman Chemical Products, Kingsport, Tenn.
7. Enjay Chemical Co., Linden, N.J.
8. B. F. Goodrich Chemical Co., Cleveland, O.
9. Harry T. Campbell Sons Corp., Towson, Md.
10. Hercules Powder Co., Wilmington, Del.
11. Hooker Chemical Co., Niagara Falls, N.Y.
12. J. M. Huber Corp., New York, N.Y.
13. Monsanto Chemical Co., Akron, O.
14. M and T Chemical Co., Rahway, N.J.
15. Nalco Chemical Co., Chicago, Ill.
16. Naugatuck Chemical Co., Naugatuck, Conn.
17. Neville Chemical Co., Pittsburgh, Pa.
18. Nuodex Products Co., Elizabeth, N.J.
19. Oils, Inc., Patterson, N.J.
20. Phillips Chemical Co. (Rubber Chemicals Div.), Akron, O.
21. Pittsburgh Plate Glass Co., Pittsburgh, Pa.
22. Sartomer Resins, Inc., Philadelphia, Pa.

No.

23. Schenectady Varnish Co., Inc., Schenectady, N.Y.

24. Sierra Talc and Clay Co., South Pasadena, Calif.

25. Sun Oil Co., Philadelphia, Pa.

26. Thiokol Chemical Corp., Trenton, N.J.

27. Titanium Pigment Corp., New York, N.Y.

28. Union Carbide Corp., New York, N.Y.

29. Union Carbide Corp. (Linde Division), Tonawanda, N.Y.

30. Universal Oil Products, Des Plaines, Ill.

31. Upjohn Co., Kalamazoo, Mich.

32. R. T. Vanderbilt Co., Inc., New York, N.Y.

APPENDIX III

Standard Test Methods

Federal Test Method Std. No. 601	Method Number
Tensile Strength	4111
Ultimate elongation	4121
Stress at 300% elongation	4131
Hardness	3021
Volume swell	6211
Specific gravity	14011
Federal Test Method CCC-T-191b	
Accelerated weatherometer exposure	5670
Soil burial resistance	5762
Water leaching resistance	5830
A.S.T.M. Standards	**ASTM Designation**
Abrasion resistance, NBS	1630
Compression-set resistance	395
Cut-growth resistance	1052
Fungal resistance	1924
Gehman low-temperature stiffness	1053
Expanded cellular rubber properties	1056
Low-temperature retraction	1329
Mooney viscosity, scorch and cure index	1646
Ozone resistance	1149
Tear resistance (die "C")	624
Test sheet preparation	15
Weathering resistance	518

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SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPD) RUBBERS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(Last name, first name, initial)*
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12. SPONSORING MILITARY ACTIVITY Rubber, Plastics & Leather Engineering Br., Clothing & Organic Materials Div., U. S. Army Natick Laboratories, Natick, Mass. 01762

13. ABSTRACT

High quality ethylene-propylene diene (EPD) rubber vulcanizates can be produced by using hydrated silica as the reinforcing filler. Modification of EPD rubber by chemical promotors such as p-quinone dioxime and the use of silica activators such as polyethylene glycol gives compounds with an acceptable rate of cure. Hot mastication, especially in the presence of halogenated compounds, gives vulcanizates with good physical properties. Processing aids such as stearic acid may be used, and oil-extended EPD rubber is a convenient plasticizer for silica-reinforced compounds.

To reduce costs, silica fillers can be extended with other such low-cost fillers as hard clay. EPD rubbers may also be blended with other elastomers. High quality silica-reinforced expanded EPD rubbers may be produced by conventional blowing agents and processing techniques. Silica-reinforced EPD rubbers crosslinked with organic peroxides give vulcanizates with good resistance to abrasion and compression set.

EPD rubber vulcanizates have excellent resistance to ozone and fungi and, in the presence of ultraviolet screening agents, show good weathering properties. It is expected that, in the future, ethylene-propylene diene rubbers will have many applications in military equipment.

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Unclassified

APPENDIX 19 SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPDM) RUBBERS

19b Coloured EPDM Compounds - Laboratory Records, 30 September, 1964 and Formulations. 19.56 - 19.59

These records are copied from Notebook Number 3764, pages 17 and 18 issued by Quartermaster Research and Engineering Command, US Army, Natick, Massachusetts, USA. The entries were made by the author and "disclosed to and understood by" the coworker, Vincent S. Javier. The entries, made on 30 September 1964, relate to formulations developed for high quality, silica-reinforced, ethylene-propylene diene vulcanizates designed for use in long-term ageing studies.

Specimens of EPDM vulcanizates produced to the requirements of these formulations, are given at Appendix 28b.

QUARTERMASTER RESEARCH & ENGINEERING COMMAND, US ARMY

17
NOTEBOOK NUMBER
3762.

SUBJECT: Coloured EPT compounds [EPT 92, 189-193]

DATE: Sept 30, 64.

PROJECT NUMBER

In order to evaluate the outdoor weather resistance (and gore resistance) of coloured EPT compounds the following materials were made -

Number EPT	92	189	190	191	192	193
Colour	Black	Red	White	Olive Drab	Light Grey	Dark Grey
Ardel 1020	80	80	80	80	80	80
Epalene X400	40	40	40	40	40	40
Epolen 40	4.5	4.5	7.5	7.5	7.5	7.5
FMF	1	1	—	1	1	1
Ultrawax 4000	1	1	1	1	1	1
Stearic acid	1	1	1	1	1	1
Sil-Co-Sil 233	50	50	42	50	42	50
Titanium dioxide (RHD)	—	—	14	—	14	5
Sterling NS Black HAF	3	—	—	—	—	—
Raven 33 Black	—	—	—	—	—	1
Red Iron Oxide Pure	—	6	—	—	—	—
Olive Drab Pigment*	—	—	—	8	—	—
CSP	—	—	1.5	—	—	—

Compounds Hot milled 10'/320°F. All compounds containing FMF darken on hot milling.

Curing system: Zinc oxide 5, sulphur 2, methyl tuads 0.75, Ethyl A 0.75, MBT 1.5.

Compounds Cured 20'/320° on Tenax sheets for exposure.

Olive Drab Pigment : Chrome Green 85 S Reynolds
Red Iron Oxide Pure 12.5 "
P33 Black 2.0

SIGNATURE: D. Dissen

DATE: Sept 30, 64

DISCLOSED TO AND UNDERSTOOD BY: Vincent L. Jarvis

DATE: 3 Sept 64

DISCLOSED TO AND UNDERSTOOD BY WITNESS:

DATE

QUARTERMASTER RESEARCH & ENGINEERING COMMAND, US ARMY

19
NOTEBOOK NUMBER 3762

OBJECT: Typical Properties of Selected EPT Cpds [EPT 92, 189-193]
DATE: Sept 30/64
PROJECT NUMBER:

All compounds cured 20'/330°F.

AS MOLDED

Compound and Color	T.S.	Eb	M300%p.	Dur A
EPT 92 BLACK	3600	540	1225	59
EPT 189 RED	3200	550	1100	57
EPT 190 WHITE	3200	640	575	56
EPT 191 O. DRAB	3550	560	1000	59
EPT 192 LIGHT GREY	3000	570	900	57
EPT 193 DARK GREY	3300	560	1150	58

HEAT AGED 16 HOURS/100°C No change in cdn on aging

EPT 92	3400	460	1800	62
EPT 189	3300	470	1550	60
EPT 190	2650	510	850	57
EPT 191	3300	500	1550	60
EPT 192	2950	470	1350	56
EPT 193	3200	470	1550	61

In all cases heat aging improves the 300% modulus by about 50%

SIGNATURE: P. Lauer

DISCLOSED TO AND UNDERSTOOD BY WITNESS: Vincent B. James
DATE: 30 Sept 64

DISCLOSED TO AND UNDERSTOOD BY WITNESS:
DATE: Sept 30/64

APPENDIX 19b

FORMULATIONS OF EPT AND NITRILE-PVC COMPOUNDS

1. EPT Compounds (EPT 92 and 189-193)

1.1 Base Formulation

	Parts by weight
Ethylene-propylene diene rubber, Nordel 1040	80
Ethylene-propylene diene rubber, oil extended, Royalene X 400	40
Chlorosulphonated polyethylene, Hypalon 40	7.5
Polyethylene glycol 4000	1.0
Stearic acid	1.0

1.2 Individual Formulations

EPT Number	92	189	190	191	192	193
p-Quinone dioxime	1	1	-	1	1	1
Silica, Hi-Sil 233	50	50	42	50	42	50
Carbon black, HAF	3	-	-	-	-	-
Red iron oxide, pure	-	6	-	-	-	-
Titanium dioxide, RA40	-	-	14	-	14	5
Octachlorocyclopentene, C58	-	-	1.5	-	-	-
Olive-drab pigment*	-	-	-	8.0	-	-
Carbon black, P33	-	-	-	-	-	1.0

The compounds mixed with activators, fillers and pigments were hot-milled at 160°C for 10 min, cooled and the curing system added.

1.3 Curing System

Zinc oxide	5.0
Sulphur	2.0
Tetramethylthiuram disulphide, TMTD	0.75
Dipentamethylenethiuram tetrasulphide, DPMTT	0.75
2- Mercaptobenzothiazole, MBT	1.5

All compounds were cured at 160°C for 20 min.

*Olive-drab pigment:	Chrome green	85.5
	Red iron oxide, pure	12.5
	Carbon black, P33	2.0

2. Nitrile-PVC Compounds (Ozo 194)

Ingredient	Parts by weight
Nitrile-PVC rubber, Paracril Ozo	100
Terpene-resin acid blend, Turgum S	3
Zinc oxide	3

Ingredient	Parts by weight
Stearic acid	1.5
Reinforcing silica, Hi-Sil 233	45
Carbon black, Philblack 0	3
Wax blend, Sunproof Jr.	1
Diethylene glycol	3
Dioctyl phthalate	12.5
Polyether plasticiser, Thiokol TP110	12.5
2- Mercaptobenzothiazole, MBT	1.5
Benzothiazyl disulphide, Altax	0.5
Zinc dimethyldithiocarbamate, ZDC, Methazate	0.5
Di - orthotolylguanidine, DOTG	0.5
Sulphur	1.5
Antioxidant, Octamine*	

*Reaction product of diphenylamine and diisobutylene

The compound was cured at 160°C for 10 min.

APPENDIX 19 SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPDM) RUBBERS

19c Properties of EPDM Rubbers after Indoor Ageing 19.61

(i) After six years

Test results were issued in September, 1970 by W.H. Meek for Head, Force and Temperature Group, Materials Research Laboratories, Melbourne, under their reference T 70-237. Units used at that time have not been changed.

(ii) After thirteen years

Test results were issued in January, 1978 by N. Browne for Head, Textiles Group, Materials Research Laboratories, Melbourne under their reference POL 78/1. For comparison with earlier testing results, traditional units have been retained.

See also Appendix 28a.

APPENDIX 19c PROPERTIES OF RUBBERS AFTER INDOOR STORAGE

Number	Compound and Colour	Property		"As moulded" (9/64)	After storage 6 yr (9/70)	After storage 13.3 yr (1/78)
EPDM 92	EPDM Black	TS	lbf/in^2	3500	3530	3700
		EB	per cent	540	510	500
		M300	lbf/in^2	1225	1710	1810
		H	A scale*	59	66	67
189	EPDM Red	TS		3200	3420	3420
		EB		550	520	510
		M300		1100	1420	1550
		H		57	62	65
190	EPDM White	TS		3300	2900	2980
		EB		640	590	570
		M300		575	840	900
		H		56	63	65
191	EPDM Olive-drab	TS		3550	3560	3560
		EB		560	560	550
		M300		1000	1330	1400
		H		59	62	65
192	EPDM Light-grey	TS		3000	3030	2450
		EB		570	530	470
		M300		900	1280	1290
		H		57	62	63
193	EPDM Dark grey	TS		3300	3320	3130
		EB		560	540	510
		M300		1150	1320	1380
		H		58	62	63
OZO 194	Nitrile-PVC Black	TS		1850	2550	1880
		EB		620	470	310
		M300		750	1690	1880
		H		71	84	89

* Instant reading of Durometer on ends of 3 dumb-bells layered up.
Temperature during conditioning and testing, 22°C.

APPENDIX 20 THE TROPICAL DETERIORATION OF RUBBER

20a The Tropical Deterioration of Rubber
P. DUNN and S.J. HART.
Journal of the IRI,
3, No. 2, 1 (1969). 20.2 - 20.8

20b The Weathering of Vulcanized Rubbers
P. DUNN and S.J. HART
Report 408. Defence Standards
Laboratories, Department of Supply,
Melbourne, Australia. 20.9 - 20.10

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Volume 3 Number 2 April 1969

The Tropical Deterioration of Rubber

By: P. DUNN and S. J. HART

Australian Defence Scientific Service,
Defence Standards Laboratories
Maribyrnong, Victoria, Australia.

APPENDIX 20a
p.20.2-20.8

The Tropical Deterioration of Rubber

By P. DUNN and S. J. HART

Department of Supply, Australian Defence Scientific Service, Defence Standards Laboratories, Maribyrnong, Victoria

Presented at the First Australian Rubber Technology Convention of the Institution of the Rubber Industry (Australasian Section), Terrigal, NSW, September 1968

SUMMARY

The facilities in Australia for the tropical testing of rubber and similar materials which are operated by the United Kingdom and Australian Governments, are described. Details are given of some tropical exposure trials being undertaken on rubbers and similar materials, with especial reference to current trials.

The current and continuing trial on the tropical deterioration of ethylene-propylene diene rubber vulcanisates is described. Details are given of the types of vulcanisates under investigation, of the effects of twelve months' exposure on stressed and unstressed specimens at various sites and of preliminary experiments to correlate accelerated ageing with outdoor exposure.

INTRODUCTION

ORGANIC materials are susceptible to attack by fungi, bacteria, insects and rodents as well as to ultraviolet radiation and other factors associated with weathering. The microbiological deterioration of rubbers and plastics has been discussed in a recent comprehensive review of Heap[1], and others[2, 3] while Pacitti[4] has reviewed the attack of rubbers and plastics by other agents, such as insects and rodents. The recent books by Rosato and Schwartz[5, 6] and the symposium report by Kamal[7] describe many environmental effects on organic materials, and their conclusions are, in general, applicable to the deterioration of many elastomers.

Every year much military material is damaged, destroyed or made unsafe because of microbiological attack. Organic materials in the form of plastics, rubbers, adhesives, paints, fuels, lubricants, textiles and food are all susceptible to fungal deterioration. Failures or defects in military equipment operating in tropical areas during World War II, and more recently in Vietnam has necessitated a marked increase in studies of tropical deterioration. Increasing usage of plastics and elastomers in both military and commercial equipment has intensified this need.

All the factors causing the deterioration of materials are not known, so while it is possible to carry out laboratory tests to determine effects of temperature, humidity, fungal and bacterial attack, artificial ageing, ozone etc, it is still necessary to undertake outdoor exposure tests in areas where adverse conditions are common.

Following the closure in 1958, of the United Kingdom Tropical Test Station in Nigeria, it was agreed that Great Britain and Australia would co-operate in setting up exposure facilities in the tropical areas of Australia. The Joint Tropical Research Unit, JTRU, was formed and the buildings occupied late in 1962. The Unit is jointly financed by the two Governments and the staff consists of both British and Australian personnel. The Ministry of Technology, acting through the Explosives Research and Development Establishment (ERDE), Waltham Abbey, UK, and the Department of Supply, acting through the Defence Standards Laboratories (DSL), Maribyrnong, Victoria, are the agencies of the two Governments. JTRU is under the operational control of the Chief Superintendent, DSL.

Although the work of JTRU is primarily concerned with the study of materials of interest to the Services, trials for commercial organisations may be conducted on a charge basis.

Broadly the functions of JTRU are to study the behaviour and causes of degradation of materials and stores in tropical environments, and means of its prevention. This includes studies of materials which have performed successfully under simulated laboratory conditions, but which fail during tropical exposure.

JTRU has four main sites in Northern Queensland. The site at Innisfail, latitude 17° 32'S, occupies some 90 acres of tropical secondary rain forest. About two acres have been cleared to house the laboratories, the exposure racks (open site) and the meteorological instruments. The cleared area is suitable for the study of the effects of tropical weather on materials, while the jungle site enables the additional effects of vegetation, termites, fungi and other microbiological life to be studied.

There is also a hot dry site at Cloncurry, latitude 20° 43'S, some 300 miles south-west of Innisfail, and a marine immersion site at Clump Point, near Innisfail. At the marine site the samples can be immersed in sea water of world average salinity and temperature varying from 24° to 32°C.

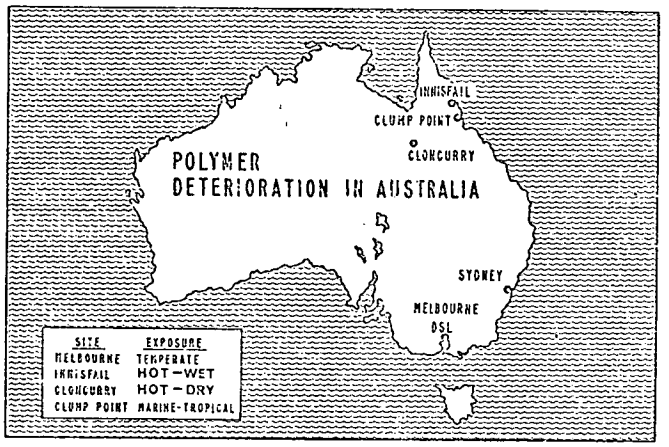

Fig. 1

The JTRU staff are usually located at Innisfail, but visit the other sites at frequent intervals. Exposure of materials under temperate conditions is also made for comparison in Britain by ERDE and in Australia, by DSL, at Maribyrnong about 2,000 miles south of Innisfail.

The locations of the various sites in Australia are shown in Fig. 1. Meteorological data for the year 1967 are summarised in Table I. Detailed monthly records for each site for 1967 are also available if required.

TABLE I —Typical Average Meteorological Data for Exposure Sites—1967

Condition	*Melbourne Victoria Temperate*	*JTRU, Innisfail Open Site Hot/Wet*	*JTRU, Innisfail Jungle Site Hot/Wet*	*JTRU, Cloncurry Hot/Dry*
Temperature, °F				
Average Daily Maximum	67·9	81·6	78·2	90·2
Average Daily Minimum	50·9	66·1	66·1	66·4
Relative Humidity, %				
Average Daily Maximum	53*	93	97	49
Average Daily Minimum		53	79	21
Precipitation, inches				
Total Rainfall	13**	145	—	13·5
Radiation				
Total Sun Hours ... ... (Campbell-Stokes)	2,304	2,585	—	3,557

*Average relative humidity, % at 1,500 hr.
**This figure is not typical, as 1967 was a year of drought.
The long term average rainfall for Melbourne is 26 inches per year.

Since the Unit started six years ago, nearly fifty exposure and storage trials have been commenced on a range of materials. Typical aims of these trials have been to determine the corrosion resistance of various metals, the resistance of metals to stress cracking under hot/wet conditions, the resistance of paints, the ageing characteristics of rubbers in hot/wet and hot/dry storage, the resistance of plastics to deterioration by fungi and weather, and the resistance of coated timber to attack by marine boring organisms.

A survey has been made of the termite population at the Innisfail site and the microbiological flora at both the cleared and jungle sites is being determined. Information is being gathered about the corrosivity of the sites at Innisfail and Cloncurry.

CURRENT TROPICAL TRIALS ON RUBBERS

At present a total of five trials concerned with rubbers and related materials are being undertaken at JTRU. Of these two are arranged by ERDE, one by the Rubber and Plastics Research Association (RAPRA) UK and two by DSL. Summary details of these trials are given in Table II.

TABLE II—Current Trials on Rubber at JTRU

Trial	*Purpose*	*Originator*	*No. of Samples*	*Duration (Years)*	*Location*
Rubber and related elastomers	Comparison of rates of degradation of various elastomers when exposed under tropical conditions and correlation with behaviour under temperature exposure and controlled laboratory conditions	United Kingdom	378	8	Innisfail Cloncurry
Polyurethane rubbers	Behaviour under tropical conditions of polyether and polyester urethanes exposed stressed and unstressed	United Kingdom	420	2–3	Innisfail Cloncurry
Twenty year storage—rubber ageing trial	Various plastics and rubber components, some under compression are being stored to assess changes with time of different formulations	RAPRA (U.K.) FRADA (U.K.)	864 boxes	20	Innisfail Cloncurry
Marine immersion	Sea water immersion of wooden panels coated with various plastics and rubbers	Australia Defence Standards Laboratories	48	2–3	Clump Point
Ethylene-propylene diene rubbers	Evaluation of silica reinforced EPD rubbers for outdoor weather resistance. SBR and nitrile-poly (vinyl chloride) rubbers are included as controls	Australia Defence Standards Laboratories	200	2–4	Innisfail Cloncurry Melbourne

The tropical trials arranged by ERDE cover studies on the deterioration of general purpose natural and synthetic rubbers, and the breakdown of polyester and polyether urethane rubbers.

In 1958, the Australian Government made exposure facilities available for a 20-year natural ageing programme sponsored by RAPRA. Facilities for exposure under hot/dry conditions were arranged at Cloncurry and under hot/wet conditions at Cairns in North Queensland. In 1964, the samples exposed at Cairns were transferred to JTRU, Innisfail, which is located 60 miles to the south and has a similar climate.

Following initial studies at RAPRA a total of nineteen different rubbers and six different plastics were selected for trial. The specimens were mounted in thirty-three identical ventilated aluminium boxes for indoor storage at the selected sites. Specimens exposed in Australia were returned to RAPRA at selected intervals for evaluation. Tests such as tensile strength, modulus at 300 per cent elongation, compression set, hardness, elongation at break, low temperature resistance, resilience, electrical resistivity and volume swell were used to determine changes in the specimens as a result of long-term storage. The report by Moakes[8] summarises the results of these trials up until 1966.

Some specimens submitted by the Factice Research and Development Association (UK) were also exposed at the same time as the samples supplied by RAPRA. Further details on these trials can be obtained from RAPRA and FRADA.

The effect of sea-water immersion at Clump Point on wooden panels of Khaya Ivorensis (West African Mahogany), coated with various rubbers and plastics, has also been investigated. Coatings included reinforced and unreinforced epoxy and polyester resins, polychloroprene rubber and chlorosulphonated polyethylene rubber. Some of the panels, as well as their coatings, contained organic toxins in order to reduce the attack by marine borers and the effect of marine fouling organisms. A second marine immersion trial commenced early in 1968 and will continue for at least two years. Panels impregnated with organotin compounds and coated with polychloroprene rubber show good resistance to marine borers and some resistance to marine fouling.

Because of the military potential of ethylene-propylene diene (EPD) rubber vulcanisates, a trial has been arranged by DSL to investigate the resistance of these materials to tropical deterioration.

TROPICAL DETERIORATION OF EPD RUBBERS

There is a continuing need for high quality black and non-black rubber vulcanisates for military use. General purpose vulcanisates should be capable of use over the temperature range −50°C to +150°C, and should have good long-term ozone, ageing and weathering resistance. Vulcanisates based on EPD rubber appear to meet these requirements and are being investigated.

As reported previously[9], EPD rubbers can be compounded to give vulcanisates with good resistance to heat, ozone, water and steam, and with excellent electrical and dynamic properties as well as good resistance to ageing and weathering. Carbon black reinforcement of EPD rubbers gives vulcanisates with high modulus and tensile strength. To obtain equivalent performance in non-black compounds it is necessary to use hydrated silica as the reinforcing agent.

Compounds for Evaluation

In order to compare the weather resistance of vulcanisates from EPD rubbers to that of other synthetic rubbers, a total of eight different vulcanisates were formulated in the hardness range 61–68 IRHD. Formulations and properties are given in Tables III, IV and V and are summarised at the top of page 83.

TABLE III—SBR and Carbon Black-Reinforced EPD Rubbers

Compound No.	*A*	*B*	*C*
EPD Rubber (' Nordel ' 1040)	—	—	80
SBR 1502	90	100	—
EPD Rubber (' Royalene ' 400)	20	—	40
Light process oil	—	10	—
Silica Filler (' Hi-Sil ' 233)	45	45	—
Chlorosulphonated polyethylene	—	—	7·5
HAF Black	3	3	53
Polymerised trimethyl dihydroquinoline	1	1	—
Zinc Oxide	1	1	5
Sulphur	3	3	2
Benzothiazyl disulphide	1·5	1·5	—
Di-orthotolyiguanidine	0·75	0·75	—
TMTD	—	—	0·75
DPMTT	0·5	0·5	0·75
MBT	—	—	1·5
Stearic acid	—	—	1
N,N'-bis(1-methylheptyl)p-phenylenediamine	3	3	—
All compounds mixed on a warm mill with no water cooling			
Cure: minutes at °C	15/164	15/154	20/160
Properties (as moulded):			
Tensile strength, psi	2,500	2,700	2,300
Ultimate elongation, %	620	680	430
Stress at 300% elongation	700	600	1,400
Hardness, IRHD	68	62	66
Compression set, % after:			
24 hr at RT	6·3	18·0	14·2
24 hr at 100°C	68·6	86·0	60·2
Ozone resistance, 50 pphm at 38°C, bent loop, hr to crack	1,000+	12	1,000+

TABLE IV—Black and White Silica-Reinforced EPD Rubbers

Compound No.	*E*	*F*	*G*	*L*
EPD Rubber (' Nordel ' 1040)	80	80	80	80
EPD Rubber (' Royalene ' 400)	40	40	40	40
Chlorosulphonated polyethylene	7·5	7·5	7·5	7·5
Silica filler (' Hi-Sil ' 233)	50	50	50	42
Polyethylene glycol	1	1	1	1
p-Quinone dioxime	1	1	—	—
HAF Black	3	3	3	—
Stearic acid	1	1	1	1
Time of hot milling (min at °C)	10/160	10/160	10/160	10/160
Titanium dioxide pigment	—	—	—	16
Dicumyl peroxide (40%)	9	—	—	—
Trimethylol propane trimethacrylate	3	—	—	—
Zinc oxide	—	5	5	5
Sulphur	—	2	2	2
TMTD	—	0·75	0·75	0·75
DPMTT	—	0·75	0·75	0·75
MBT	—	1·5	1·5	1·5
Polymethyl polyphenylisocyanate	—	—	3	—
Cure: Min at °C	20/160	20/160	20/160	20/160
Properties (as moulded):				
Tensile strength, psi	2,100	3,225	3,100	3,000
Ultimate elongation, %	610	580	600	660
Stress at 300% elongation	750	1,100	1,050	650
Hardness, IRHD	61	62	65	61
Compression set, % after:				
24 hr at RT	11·8	8·6	11·3	16·0
24 hr at 100°C	28·7	71·0	69·8	71·0
Ozone resistance, 50 pphm at 38°C, bent loop, hr to crack	1,000+	1,000+	1,000+	1,000+

All the vulcanisates were formulated to have good resistance to indoor storage and to outdoor exposure. For comparison purposes, the vulcanisates with the exception of Compound N were formulated with similar hardness properties and with similar rubber hydrocarbon volumes.

Oil-extended EPD rubber was used in Compound A after laboratory tests had shown that its use greatly improved the ozone resistance of typical SBR vulcanisates such as Compound B.

Compound	A	B	C	E	F	G	L	N
Polymer	SBR-EPDR(OE)	SBR	EPDM blend	EPDM blend	EPDM blend	EPDM blend	EPDM blend	NBR/PVC
Colour	Black	Black	Black	Black	Black	Black	White	Black
Reinforcing agent	Silica	Silica	Carbon Black	Silica	Silica	Silica	Silica	Silica
Curing system	Sulphur	Sulphur	Sulphur	Peroxide	Sulphur	Sulphur	Sulphur	Sulphur
Special activators	No	No	Yes	Yes	Yes	Yes (2)	Yes	Yes
Special additives								
Antioxidant	Yes	Yes	No	No	No	No	No	Yes
Antiozonant	Yes	Yes	No	No	No	No	No	No
Anti flex cracking agent	No	No	No	No	No	No	No	Yes
Hardness, IRHD	68	62	66	61	62	65	61	67
Specific gravity	1·07	1·07	1·04	1·05	1·06	1·05	1·1	1·29
Rubber hydrocarbon volume, %	73·3	73·8	67·6	66·5	68·2	67·6	69·0	58·0

TABLE V—Black, Silica-Reinforced Nitrile—PVC Rubber—Compound N

Butadiene-acrylonitrile rubber (' Krynac ' 800)	70
Poly(vinyl chloride)	30
MC sulphur	0·75
Dibasic lead phosphite paste	2
Polymerised 1,2-dihydro 2,2,4-trimethyl quinoline	1
Diphenylamine-diisobutylene adduct	1
Stearic acid	1·5
Zinc oxide	3
Carbon black (' Acarb ' 600)	3
Silica filler (' Neosyl ' standard)	55
Diethylene glycol	2
Tritolyl phosphate	14
Dibutyl carbitol formal	14
Cashew phenolic resin	10
MBTS	1·25
MBT	0·75
DPG	0·90
ZDC	0·25
Cure: 10 min at 160°C	
Properties (as moulded):	
Tensile strength, psi	1,850
Ultimate elongation, %	550
Stress at 300% elongation, psi	1,250
Hardness, IRHD	67
Compression set, % after	
24 hr at RT	16·0
24 hr at 100°C	71·0
Ozone resistance, 50 pphm at 38°C, bent loop, hr to crack	200+

The EPD rubber blends consisted of mixtures of unextended and oil-extended polymers. Compound C was a cold-milled, carbon black reinforced rubber activated with chlorosulphonated polyethylene and containing a conventional sulphur curing system. The remaining EPD rubbers were hot-milled, silica reinforced compounds containing several different activators. Compound E was cured with a peroxide and F, G and L contained a curing system similar to that used in Compound C. Compound L was similar to F, but had the carbon black pigment (3 phr) and part of the silica replaced by titanium dioxide to give an all-white compound.

Compound N was a silica-reinforced nitrile-poly(vinyl chloride) formulation developed at DSL for use in military footwear.

The compounding materials used were commercial products obtained from recognised suppliers. Details are given in Appendix I. Other compounding materials comparable in chemical composition and activity should prove to be equally satisfactory.

All of the rubber compounds were processed on conventional rubber compounding equipment. Whenever possible, rubber masterbatches were mixed on a 20- by 10-inch variable-speed two-roll mill, while hot mixing and final compounding were carried out on 12- by 6-inch two-roll mills. Test sheets were vulcanised in 4-cavity chrome-plated moulds in a steam-heated press.

Standard testing equipment was used. The test methods are listed in Appendix II.

Fungicidal activity of specimens after two years indoor storage was determined on 1 inch diameter test pieces stamped from tensile sheets. These were laid on sterile plates of Czapek-Dox Agar with sucrose, as reported by Smith[10], and inoculated by spraying with pure spore suspensions of fungi. Specimens incubated at 30°C and 95 per cent relative humidity were assessed after 4, 14, 28 and 56 days. The pure spore suspensions used were, *Aspergillus niger* (DSL Culture No 428), *Aspergillus Flavus* (DSL Culture No 283) and *Syncephalastrum sp* (DSL Culture No 427).

Exposure of Specimens

Samples of vulcanisates were exposed at the available sites at Innisfail, Cloncurry, Clump Point and Maribyrnong. Specimens for exposure were either in the form of tensile test sheets (6 in × 6 in × 0·075 in thick) or slabs moulded for cut growth tests (6 in × 3·5 in × 0·25 in thick). Tensile sheets were unstressed and mounted in aluminium alloy frames.

The cut growth slabs were stressed by bending around a half section of a 4 inch diameter aluminium alloy pipe. Under these conditions the initial average stress on the outer surface of the specimens was 7 per cent. At the open sites all specimens were mounted facing north at an angle of 45°. At the jungle site the specimens were mounted vertically in order to avoid contamination by leaves and other debris.

Tensile sheets were also fixed to aluminium plates and immersed in the sea at Clump Point. Others were fixed to wooden panels and buried in a termite infested area at Cloncurry.

Prior to outdoor exposure the specimens were stored indoors, in the dark, for two years at DSL, Maribyrnong. This enabled the effects of long term storage to be investigated and minimised the effect of continued cure after moulding. At present (July, 1968) the vulcanisates have been exposed outdoors for about 13 months, and the trial is expected to continue for at least another twelve months.

Results and Discussion

The properties of the vulcanisates in the " as-moulded " condition (Tables III, IV and V) indicated that acceptable properties were obtained with the formulations used, and that the state-of-cure, as measured by the Monsanto Rheometer, was adequate.

Indoor exposure of unstressed specimens showed that all the EPD rubbers were very stable and only minor changes in the physical properties of the vulcanisates were observed. Both the SBR vulcanisates (A and B) showed marked changes in physical properties during indoor storage, especially in modulus at 300 per cent elongation and in hardness. The nitrile-poly(vinyl chloride) vulcanisate (N) also showed a marked change in hardness during storage.

The physical properties of the vulcanisates after outdoor exposure for approximately 12, 30 and 52 weeks at the four exposure sites are given in Tables VI-XIII. The tensile data obtained from exposed, unstressed tensile sheets, indicated that all the vulcanisates retained acceptable physical properties. There was also no evidence of any ozone cracking or of any fungal attack on the tensile sheets. Examination of slabs to be used for the determination of cut

TABLE VI—Compound A: Silica-Reinforced SBR (with EPD)

Exposure Conditions	Property*	Time of Exposure—weeks (average) 12	30	52
DSL, Maribyrnong	T.S.	3,010	2,650	2,730
	E_B	510	480	490
	M_{300}	1,310	1,330	1,340
	H	75	77	78
	C.G.R.	—	125	220
JTRU, Innisfail Open	T.S.	2,800	2,800	2,720
	E_B	490	480	470
	M_{300}	1,280	1,330	1,440
	H	77	77	80
	C.G.R.	—	130	160
JTRU, Innisfail Jungle	T.S.	2,870	3,040	2,860
	E_B	510	520	520
	M_{300}	1,220	1,220	1,130
	H	75	75	76
	C.G.R.	—	190	95
JTRU, Cloncurry	T.S.	2,720	2,670	2,180
	E_B	490	470	410
	M_{300}	1,300	1,410	1,420
	H	75	78	79
	C.G.R.	—	140	175

Properties before outdoor exposure

As moulded: TS, 2500; E_B, 620; M_{300}, 700; H, 68; C.G.R., 125

After indoor storage (104 weeks): 2810 520 1240 74 105

*Code: T.S., tensile strength, psi; E_B, elongation at break, %; M_{300}, modulus at 300% elongation, psi; H, hardness, IRHD; C.G.R., cut growth resistance, Kc to 100% increase in cut length.

TABLE VII—Compound B: Silica-Reinforced SBR

Exposure Conditions	Property	Time of Exposure—weeks (average) 12	30	52
DSL, Maribyrnong	T.S.	2,360	2,570	2,410
	E_B	460	470	490
	M_{300}	1,280	1,300	1,240
	H	75	77	77
	C.G.R.	—	150	85
JTRU, Innisfail Open	T.S.	2,730	2,450	2,600
	E_B	500	480	480
	M_{300}	1,190	1,180	1,270
	H	77	78	79
	C.G.R.	—	115	85
JTRU, Innisfail Jungle	T.S.	2,400	2,600	2,450
	E_B	480	490	490
	M_{300}	1,130	1,180	1,110
	H	75	76	76
	C.G.R.	—	55	130
JTRU, Cloncurry	T.S.	2,510	2,490	2,150
	E_B	470	460	420
	M_{300}	1,240	1,280	1,340
	H	77	78	79
	C.G.R.	—	217	210

Properties before outdoor exposure
As moulded: T.S., 2700; E_B, 680; M_{300}, 600; H, 62; C.G.R., 125
After indoor storage (104 weeks): 2710; 520; 1200; 74; 105

TABLE VIII—Compound C: Carbon Black-Reinforced EPD Rubber

Exposure Conditions	Property	Time of Exposure—weeks (average) 12	30	52
DSL, Maribyrnong	T.S.	3,000	3,260	3,180
	E_B	420	440	420
	M_{300}	1,960	1,920	2,020
	H	73	73	74
	C.G.R.	—	150	110
JTRU, Innisfail Open	T.S.	3,260	2,920	2,920
	E_B	440	380	380
	M_{300}	1,950	2,160	2,210
	H	73	74	76
	C.G.R.	—	115	65
JTRU, Innisfail Jungle	T.S.	3,040	3,210	3,210
	E_B	420	440	440
	M_{300}	1,970	1,990	1,930
	H	72	73	73
	C.G.R.	—	95	165
JTRU, Cloncurry	T.S.	3,280	3,040	3,100
	E_B	410	370	390
	M_{300}	2,080	2,270	2,240
	H	72	75	77
	C.G.R.	—	130	155

Properties before outdoor exposure
As moulded: TS, 2300; E_B, 430; M_{300}, 1400; H, 66; C.G.R., 50
After indoor storage (104 weeks): 2840; 410; 1620; 72; 50

TABLE IX—Compound E: Silica-Reinforced EPD Rubber (Peroxide Cured)

Exposure Conditions	Property	Time of Exposure—weeks (average) 12	30	52
DSL, Maribyrnong	T.S.	2,560	2,600	2,720
	E_B	690	700	730
	M_{300}	750	750	790
	H	64	65	66
	C.G.R.	—	500+	500+
JTRU, Innisfail Open	T.S.	2,530	2,520	2,730
	E_B	710	730	750
	M_{300}	680	640	690
	H	66	66	67
	C.G.R	—	500+	500+
JTRU, Innisfail Jungle	T.S.	2,500	2,560	2,480
	E_B	720	740	750
	M_{300}	630	640	580
	H	63	66	64
	C.G.R.	—	500+	500+
JTRU, Cloncurry	T.S.	2,380	2,550	2,440
	E_B	660	700	710
	M_{300}	730	700	680
	H	67	67	68
	C.G.R.	—	300 for 40%	300 for 10%

Properties before outdoor exposure
As moulded: TS, 2100; E_B, 610; M_{300}, 750; H, 61; C.G.R., 500
After indoor storage (104 weeks): 2410; 690; 730; 63; 500+

TABLE X—Compound F: Silica-Reinforced EPD Rubber Sulphur Cured)

Exposure Conditions	Property	Time of Exposure—weeks (average) 12	30	52
DSL, Maribyrnong	T.S.	3,690	3,640	3,510
	E_B	550	550	520
	M_{300}	1,440	1,460	1,530
	H	68	68	70
	C.G.R.	—	235	550
JTRU, Innisfail Open	T.S.	3,580	3,450	3,120
	E_B	550	530	500
	M_{300}	1,430	1,460	1,450
	H	70	69	72
	C.G.R.	—	220	150
JTRU, Innisfail Jungle	T.S.	3,860	3,650	3,660
	E_B	590	580	610
	M_{300}	1,330	1,310	1,160
	H	68	70	69
	C.G.R.	—	154	400
JTRU, Cloncurry	T.S.	3,480	3,370	2,930
	E_B	520	500	460
	M_{300}	1,470	1,550	1,540
	H	69	72	72
	C.G.R.	—	150	300

Properties before outdoor exposure
As moulded: TS, 3225; E_B, 580; M_{300}, 1100; H, 62; C.G.R., 100
After indoor storage (104 weeks): 3310; 540; 1370; 67; 105

TABLE XI—Compound G: Silica-Reinforced EPD Rubber (with an Activator)

Exposure Conditions	Property	Time of Exposure—weeks (average) 12	30	52
DSL, Maribyrnong	T.S.	3,540	3,620	3,260
	E_B	580	550	530
	M_{300}	1,310	1,540	1,450
	H	72	72	74
	C.G.R.	—	316	350
JTRU, Innisfail Open	T.S.	3,320	3,310	3,150
	E_B	540	540	530
	M_{300}	1,330	1,380	1,350
	H	72	73	75
	C.G.R.	—	250	350
JTRU, Innisfail Jungle	T.S.	3,160	3,280	3,490
	E_B	550	580	610
	M_{300}	1,200	1,230	1,170
	H	69	72	71
	C.G.R.	—	170	380
JTRU, Cloncurry	T.S.	3,240	3,310	3,090
	E_B	530	510	500
	M_{300}	1,340	1,490	1,470
	H	73	75	76
	C.G.R.	—	217	290

Properties before outdoor exposure
As moulded: TS, 3100; E_B, 600; M_{300}, 1050; H, 65; C.G.R., 100
After indoor storage (104 weeks): 3210; 540; 1230; 70; 100

growth resistance and exposed stressed at an initial elongation of about 7 per cent, however, showed that the SBR vulcanisate Compound B, was severely attacked by ozone. Cut growth tests indicated that this compound as well as all the others still retained good resistance to flex cracking even after 52 weeks' exposure. The addition of the small quantity of the EPD rubber to the SBR (Compound A), markedly improved the resistance of the compound to attack by ozone, and no cracking was observed.

All the EPD rubber vulcanisates (Compounds C, E, F, G and L) showed good retention of properties after exposure. Vulcanisates cured with peroxides to form carbon-carbon crosslinks (Compound E) showed very high stability after exposure at all sites. The vulcanisates reinforced with hydrated silica showed stability equal to the compound reinforced solely with carbon black. The presence of small quantities of carbon black pigments (3 phr) in the silica-reinforced compounds was sufficient to give a high degree of protection against sunlight. As expected the all-white EPD rubber vulcanisate (L) showed the greatest change in properties after exposure, especially at those sites where the specimens received the greatest amount of ultraviolet radiation, such as Cloncurry.

Vulcanisates based on nitrile-poly(vinyl chloride) blend (N) showed good retention of properties after exposure at all sites. This confirmed data obtained from the field, concerning the long-term tropical performance of rubber end-items based on this formulation.

None of the specimens exposed in the jungle showed any signs of fungal attack, and this confirmed laboratory tests undertaken on samples after having been stored for two years.

TABLE XII—Compound L: White Silica-Reinforced EPD Rubber

Exposure Conditions	Property	Time of Exposure—weeks (average) 12	30	52
DSL, Maribyrnong	T.S.	2,820	2,440	2,030
	E_B	590	540	510
	M_{300}	800	890	880
	H	68	70	70
	C.G.R.	—	217	320
JTRU, Innisfail Open	T.S.	2,670	2,330	2,290
	E_B	580	540	560
	M_{300}	820	840	770
	H	69	70	70
	C.G.R.	—	270	550
JTRU, Innisfail Jungle	T.S.	3,320	3,130	3,130
	E_B	650	620	630
	M_{300}	760	790	730
	H	76	68	68
	C.G.R.	—	250	350
JTRU, Cloncurry	T.S.	1,870	1,850	1,800
	E_B	470	460	440
	M_{300}	890	960	960
	H	72	72	73
	C.G.R.	—	340	290

Properties before outdoor exposure
As moulded: TS, 3000; E_B, 660; M_{300}, 650; H, 61; C.G.R., 200
After indoor storage (104 weeks): 3150 630 780 65 160

TABLE XIII—Compound N: Nitrile—PVC Vulcanisate

Exposure Conditions	Property	Time of Exposure—weeks (average) 12	30	52
DSL, Maribyrnong	T.S.	2,210	2,170	2,090
	E_B	510	480	510
	M_{300}	1,470	1,560	1,500
	H	78	78	80
	C.G.R.	—	316	500+
JTRU, Innisfail Open	T.S.	2,130	1,960	2,070
	E_B	500	490	500
	M_{300}	1,510	1,420	1,550
	H	78	80	83
	C.G.R.	—	500+	500+
JTRU, Innisfail Jungle	T.S.	2,120	2,110	1,970
	E_B	530	540	490
	M_{300}	1,340	1,410	1,430
	H	76	79	80
	C.G.R.	—	300+	500+
JTRU, Cloncurry	T.S.	2,050	2,210	2,010
	E_B	470	440	450
	M_{300}	1,530	1,730	1,650
	H	79	82	83
	C.G.R.	—	500+	250

Properties before outdoor exposure
As moulded: TS, 1850; E_B, 550; M_{300}, 1250; H, 67; C.G.R., 200
After indoor storage (104 weeks): 2030 550 1320 77 450

Although the trial is being continued the present results give a guide to the performance expected from each type of vulcanisate. The results also indicate that the maximum deterioration occurred at Cloncurry and the minimum deterioration at the jungle site at Innisfail. Vulcanisates immersed in the sea and others buried in a termite infested area will be available shortly for evaluation.

In an attempt to develop a rapid screening test for vulcanisates prior to tropical exposure, we have submitted further samples of Compounds B, E and F to cut growth tests after various accelerated laboratory treatments. We believe this type of test could be of considerable value, in addition to tensile and hardness data, in assessing the long-term stability of vulcanisates. The results are set out below:

Treatment of Sample	Period of Treatment	Cut Growth, Kc to 100% increase in cut length B	E	F
Type	—	SBR S-cured	EPDM Peroxide cured	EPDM S-cured
Nil (control)	Nil	125	500+	100
Hot air exposure*, 70°C	3d	155	300+	—
	7d	155	300+	250
	21d	130	300+	200
Hot air* exposure, 100°C	2d	125	300	300
	4d	120	225	270
	7d	38	175	250
Ozone exposure*, 50 pphm, 38°C	1d	130	—	—
	3d	110	—	—
	7d	100	—	—
Weatherometer exposure* (Atlas Model 60 DMC-R)	200 hr	150	300+	300+
	450 hr	150	300+	300+
	900 hr	120	300+	300+
Hot water exposure,** 70°C	3d	36	300+	—
	7d	30	300+	220
	21d	11	300+	150
Water vapour exposure,** 70°C	7d	50	300+	170
	14d	40	300+	150
	21d	30	300+	150
Steam exposure,* 15 psi (temperature, 115°C)	1×1 hr	40	300+	260
	3×1 hr	31	300+	250
	5×1 hr	17	300+	240
	1×3 hr	55	—	—

*Samples exposed stressed over a 4 inch diameter aluminium mandrel.
**Unstressed samples exposed.

Vulcanisates from peroxide-cured EPD rubber retained excellent cut growth resistance after accelerated ageing. Vulcanisates from sulphur-cured EPD rubbers also retained good resistance, but were affected in varying degrees by ageing conditions such as exposure in hot air at 70° and 100°C, and exposure in water and water vapour at 70°C.

SBR vulcanisates were markedly affected by the ageing conditions used. Hot air at 100°C, hot water and water vapour at 70°C, and heating in steam for relatively short periods, all had a pronounced effect on the cut growth resistance of the vulcanisates. We believe that one or more of these conditions, especially ageing in steam, offers a convenient and rapid method of screening rubbers for resistance to deterioration. Special ancillary tests such as resistance to fungal attack, are also required.

We hope that the data obtained from the indoor and outdoor exposure trials will enable us to correlate the performance of the vulcanisates with the prediction of shelf-storage life from accelerated tests, such as those described by Thomas, Sinnott and Day[11].

CONCLUSIONS

The results so far obtained on samples which have been stored for a period in excess of that generally recommended for natural rubber, confirm our earlier view that end items made from vulcanisates based on EPD rubber are suitable for general-purpose military use.

During the three years since the compounds were first prepared, EPD rubbers with new diene monomers and different levels of unsaturation have become available. The rates of cure have been increased, but we do not expect the outdoor weather resistance of the vulcanisates to be seriously affected. Some further trials on these new EPD rubbers are proposed. The accelerated ageing methods described should enable us to select suitable new formulations for future exposure trials.

Results indicate, that using standard physical methods of assessment, all specimens should be stressed during outdoor exposure. The flex cut-growth test appears to be suitable for assessing the resistance of vulcanisates to indoor and outdoor ageing, as well as to accelerated ageing conditions.

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APPENDIX I—Compounding Materials

Material	*Trade Name*	*Supplier*
enzothiazyl disulphide	'Altax'	R. T. Vanderbilt Co.
utadiene-acrylonitrile	'Krynac' 800	Polysar
arbon black, HAF	'Philblack' O	Phillips Chemical Co.
arbon black	'Acarb' 600	Australian Carbon Black
ashew phenolic resin	'Cellobond' H831	British Resin Products
hlorosulphonated poly-ethylene	'Hypalon' 40	Du Pont, Inc.
ibasic lead phosphite	'Molliphos' Paste	Fletcher Chemical Co.
i'utyl carbitol formal	'Reomol' BCF	Geigy (Aust.) Pty. Ltd.
icumyl peroxide (40% active)	'Dicup' 40C	Hercules Powder Co.
i-orthotolylguanidine	'DOTG'	Du Pont, Inc.
ipentamethylenethiuram tetrasulphide	DPMTT, 'Tetrone' A	Du Pont, Inc.
iphenylamine-diiso-butylene adduct	'Octamine'	Naugatuck Chemical Co.
iphenylguanidine	DPG	Monsanto Chemical Co.
thylene-propylene diene rubber (EPDR)	'Nordel' 1040	Du Pont, Inc.
thylene-propylene diene rubber, oil extended (EPDR)	'Royalene' 400	Naugatuck Chemical Co.
ydrated silica	'Hi-Sil' 233	Pittsburgh Plate Glass
ydrated silica	'Neosyl' standard	Crossfield Pty. Ltd.
-Mercaptobenzothiazole	MBT, 'Vulcafor' MBT	ICIANZ
-Mercaptobenzothiazole disulphide	MBTS, 'Vulcafor' MBTS	ICIANZ
aphthenic oil (light coloured)	Light process oil	Sun Oil Co.
,N'-bis(1-methylheptyl)-p-phenylene-diamine	'UOP88'	Universal Oil Products
olyethylene glycol	'Carbowax' 4000	Union Carbide Co.
olymerised trimethyl dihydroquinoline	'Agerite' Resin D	R. T. Vanderbilt Co.
olymethylpolyphenyliso-cyanate	'Flectol' H	Monsanto Chemical Co.
oly (vinyl chloride) resin	'PAPI'	Upjohn Co.
-Quinone dioxime	'Corvic' H55/34	ICIANZ
BR1502	GMF	Naugatuck Chemical Co.
etramethylthiuram disulphide	'Philprene' 1502	Phillips Chemical Co.
itanium dioxide	TMTD, Methyl Tuads	R. T. Vanderbilt Co.
rimethylolpropane trimethacrylate	'Titanox' RA40	Titanium Pigment Corp.
ritolyl phosphate	SR350	Sartomer Resin, Inc.
inc dimethyldithio-carbamate	Plasticiser TTP	Albright and Wilson
	ZDC, Methazate	Naugatuck Chemical Co.

APPENDIX II—Standard Test Methods

Federal Test Method Std, No. 601	*Method Number*
Tensile Strength	4111
Ultimate elongation	4121
Stress at 300% elongation	4131
Hardness	3021
ASTM Standards	*ASTM Designation*
Compression-set resistance	D 395
Cut-growth resistance	D1052
Ozone resistance	D1149
Test sheet preparation	D 15
Weathering resistance	D 518
Weatherometer exposure	E 42

REFERENCES

1. Heap, W. M., "Microbiological Deterioration of Rubbers and Plastics." Rubber and Plastics Research Association of Great Britain, Shawbury. Information Circular No. 476 (1965).
2. MacLachlan, J., Heap, W. M. and Pacitti, J., "Attack of Bacteria and Fungi on Rubbers and Plastics in the Tropics—A Literature Review." Monograph No. 23, "Microbiological Deterioration in the Tropics." Society of Chemical Industry, London, 1966, p. 185.
3. Anon, "The Attack of Rubbers and Plastics by Bacteria, Fungi and Insects, and Methods of Prevention." Bibliography No. 67, Division of Rubber Chemistry, American Chemical Society, Akron, Ohio, 1966.
4. Pacitti, J., "Attack by Insects and Rodents on Rubbers and Plastics." Rubber and Plastics Research Association of Great Britain, Shawbury. Information Circular No. 475, 1965.
5. Rosato, D. V. and Schwartz, R. T., "Environmental Effects on Polymeric Materials." Volume I, "Environments." Interscience Publishers, New York, 1968.
6. Rosato, D. V. and Schwartz, R. T., "Environmental Effects on Polymeric Materials." Volume II, "Materials." Chapter 14 "Elastomers" by J. K. Sieron and R. G. Spain. Interscience Publishers, New York, 1968.
7. Kamal, M. R., "Weatherability of Plastic Materials." Applied Polymer Symposia, No. 4. Interscience Publishers, New York, 1967.
8. Moakes, R. C. W., "Progress in the 20 Year Natural Ageing Programme." RAPRA Bulletin, Great Britain, 1966, *20*, No. 2, 18.
9. Dunn, P. and Javier, V. S., "Silica-Reinforced Ethylene-Propylene Diene (EPD) Rubbers." Technical Report, C and OM-7. US Army Natick Laboratories, US Army Material Command, Natick, Mass., 1965.
10. Smith, G., "Industrial Mycology," Edward Arnold, London, 1954, p. 242.
11. Thomas, D. K., Sinnott, R. and Day, J., "The Prediction of Shelf-storage Life in Rubbers from Accelerated Heat Ageing Tests." Technical Report 67118. Royal Aircraft Establishment, Farnborough, United Kingdom, 1967.

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DEPARTMENT OF SUPPLY

AUSTRALIAN DEFENCE SCIENTIFIC SERVICE

DEFENCE STANDARDS LABORATORIES

REPORT 408

THE WEATHERING OF VULCANIZED RUBBERS

P. DUNN and S. J. HART

SUMMARY

Details are given of a four year trial concerned with indoor storage and outdoor exposure of some vulcanized rubbers based on carbon black or silica-reinforcing materials in styrene-butadiene rubber, ethylene-propylene diene rubber and a butadiene-acrylonitrile rubber blended with poly (vinyl chloride) resin. Storage trials for two years, followed by exposure trials, at four different sites, also for two years were carried out. Seawater immersion and soil burial trials on the vulcanized rubbers are also described.

The effect of the various environments on some of the physical properties of the vulcanizates has been studied. Some conclusions have also been drawn concerning the performance of the vulcanizates as might be expected during typical indoor storage and outdoor use.

OCTOBER, 1970

POSTAL ADDRESS: Chief Superintendent, Defence Standards Laboratories. Box 50, P.O. Ascot Vale, Victoria. 3032

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DEPARTMENT OF SUPPLY
AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
DEFENCE STANDARDS LABORATORIES

REPORT 404

DEVELOPMENT OF MAGNETIC RUBBERS

P. DUNN and J. M. D. WOODFORD

SUMMARY

Magnetic rubbers have considerable potential for use in both military and civilian applications. The development of flexible magnets based on vulcanized rubbers, containing either Australian or imported ferrites is described. Processing techniques, the effect of different elastomers on the physical and magnetic properties of the magnetic rubber and the effect of improved manufacturing techniques for the ferrites, were evaluated.

Information obtained should assist in the production of high quality, flexible, magnetic rubbers using Australian-produced ferrites.

SEPTEMBER, 1970

POSTAL ADDRESS: Chief Superintendent, Defence Standards Laboratories, Box 50, P.O., Ascot Vale, Victoria, 3032.

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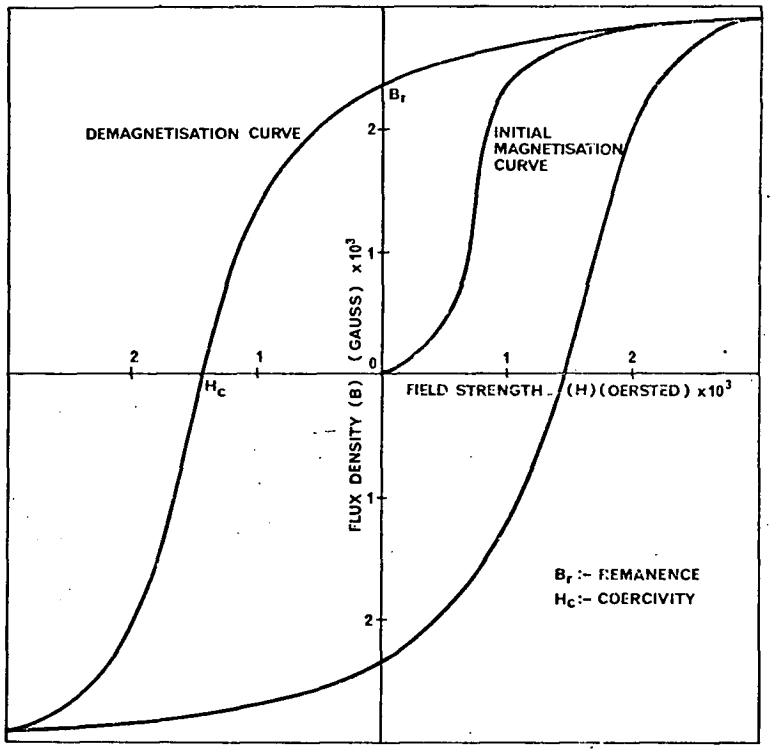
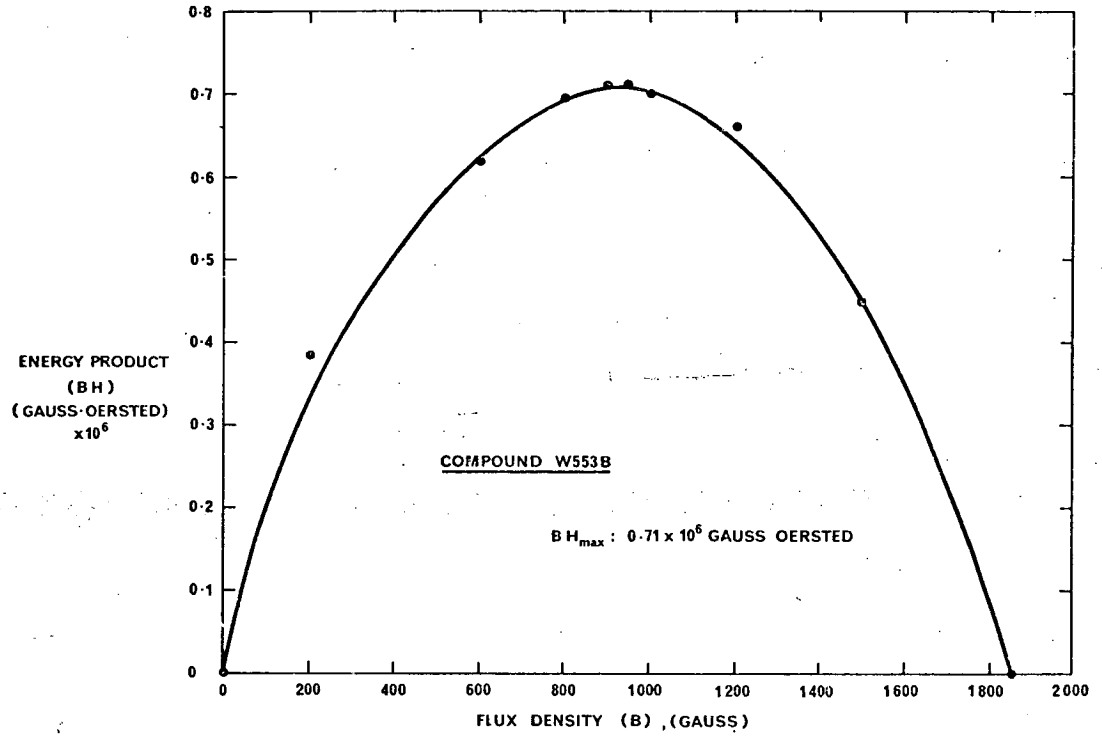
APPENDIX 21b

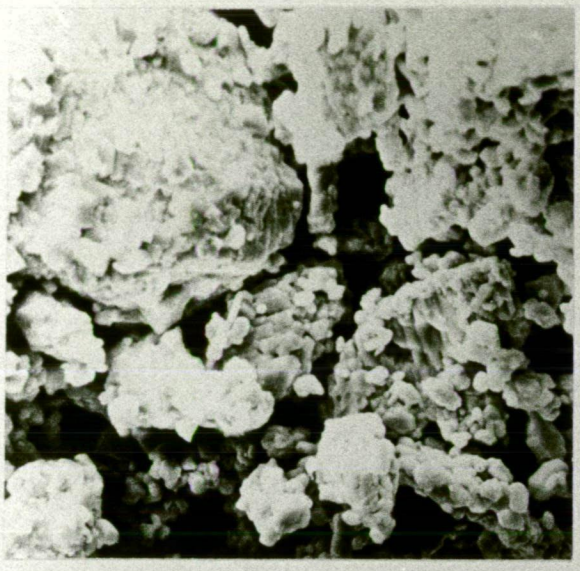


Hysterisis loop of a permanent magnet

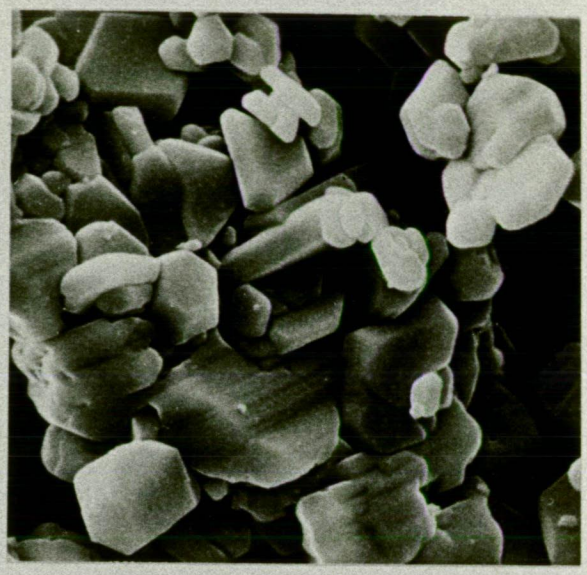
APPENDIX 21c



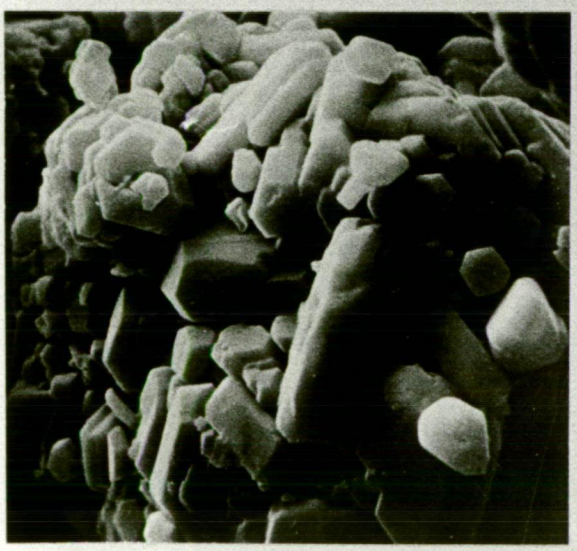
Relationship between energy product and flux density for a ferrite loaded butadiene-acrylonitrile rubber (Compound W553B)



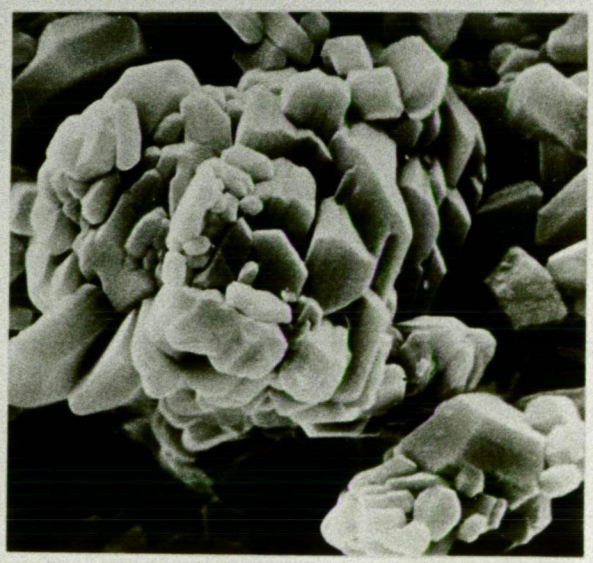
0° R/B x1000



0° R/B x 5000



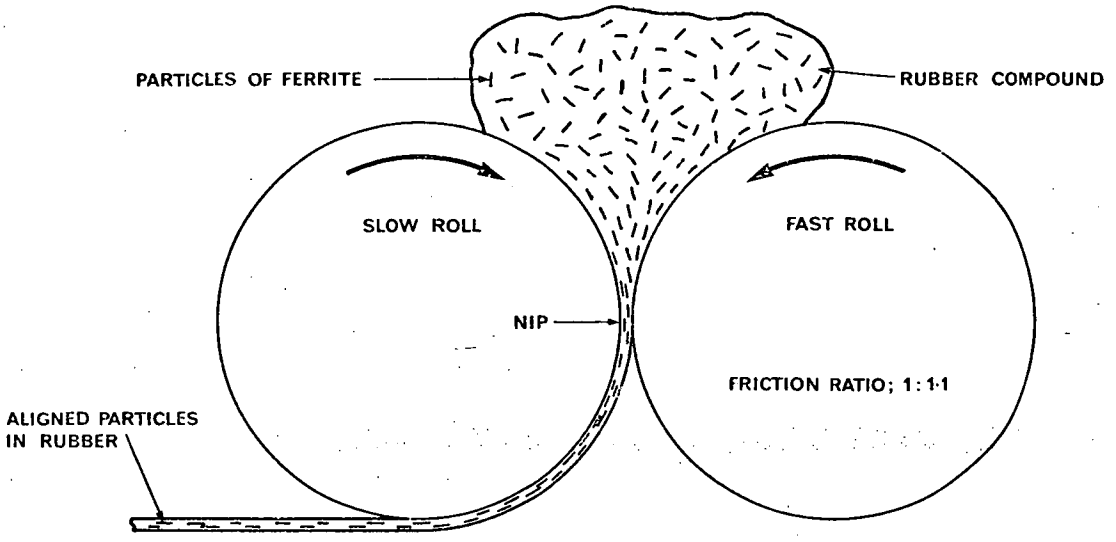
0° R/B x5200



45° R/B x 5000

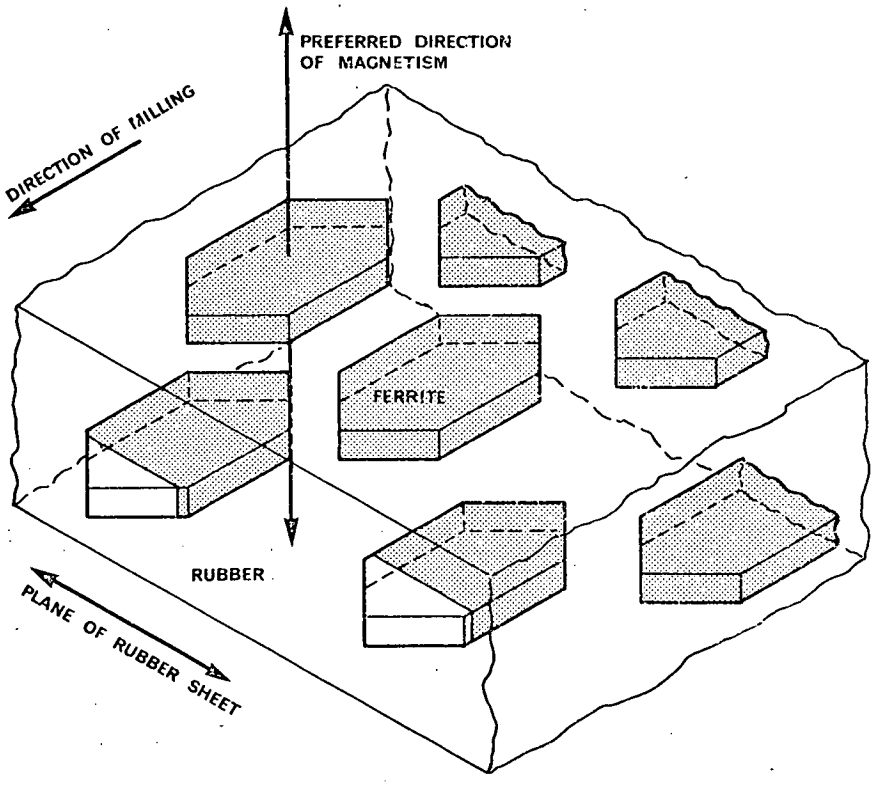
Appendix 21d - Electron micrographs of an Australian-produced ferrite (Batch R/B), showing platelet-type, crystalline structure, and aggregated particles.

APPENDIX 21e



Schematic diagram of the alignment of particles in a rubber by a 2-roll mill

APPENDIX 21f



Aligned particles of ferrite in a rubber

APPENDIX 21g

DETAILS OF A MAGNETIC RUBBER DEVELOPED AT MRL

(COMPOUND MRL-W553B)

Material	Parts by weight
Butadiene-acrylonitrile rubber (a)	76
Barium ferrite (b)	900
Sulphur	2.0
Zinc oxide	4.0
Stearic acid	1.5
4-Isopropylamine diphenylamine (c)	2.0
Mercaptobenzothiazole (d)	0.6
Diphenylguanidine (e)	0.3
Tetramethylthiuram monosulphide (f)	0.3

Cure time : 30 min at 146°C (g)

(a) Butakon A3003. ICI Australia Limited, Melbourne
(b) Batch B/5/3. Plessey Rola Pty. Ltd., Melbourne
(c) Nonox ZA)
(d) Vulcafor MBT) ICI Australia Limited, Melbourne
(e) Vulcafor DPG)
(f) Vulcafor MS)
(g) The high ferrite loading caused handling problems on the rubber mill.

Properties of barium ferrite, Batch B/5/3

Ferrite, % by weight	91.3
Ferrite, % by weight	66.0
Particle size, μm (h)	0.82
Size reduction process	Attrition
Heat treatment	Nil

(h) From Fischer Sub-Sieve Sizer measurements

Magnetic properties

Remenance, Br, gauss	1855
, mT	186
Coercivity, Hc, oersted	1460
, amp turns/m x 10^{-3}	11.6
Maximum energy product, BH max,	
gauss oersted x 10^{6}	0.71
tesla amp turns/m x 10^{3}	0.58

APPENDIX 22 IMPRINTS OF BARNACLES

22a Imprints of Barnacles
P. DUNN and GEORGE F. SANSOM 22.2 - 22.8

Draft paper prepared for publication.
Details are available from reference 259.

22b Composition of Chlorosulphonated
Polyethylene Coating Material 22.9

APPENDIX 22a

IMPRINTS OF BARNACLES

As part of an investigation of the resistance of coated timber to teredine borers (shipworms) (Appendix 12c) trials were undertaken over a period of several years on panels of *Khaya ivorensis* (West African mahogany) coated with a range of plastics and rubber materials. The materials had a wide range of hardness, and included glass reinforced plastics, coated nylon fabrics and a number of carbon black or silica-reinforced synthetic rubbers.

Timber panels, 305 mm x 147 mm x 23 mm, were conditioned by soaking in seawater at room temperature for 7d, air-dried for 14d and then coated. The coated panels were immersed at a depth of 1 m on a raft, located approximately 800 m from the coast, near Clump Point, North Queensland, Australia (latitude, 17° 56' S, longitude, 146° 19' E). At the immersion site the depth of water was about 8 m, the average water temperature, 27.2°C and the average salinity estimated as sodium chloride, 3.03%. The main immersion trial commenced late August, 1968, and was terminated late August, 1971.

On withdrawal, all panels showed heavy growths of a variety of marine fouling organisms, many of which were identified using established descriptions[1,2]. Of the barnacles present, the most common and the only species positively identified was *Balanus amphitrite* (Darwin). Removal of the marine fouling by physical means showed that the barnacles, although strongly adhering in many cases, could generally be removed without damage to the surface of the coating. Of all the coatings examined, only chlorosulphonated polyethylene showed physical evidence of any change in the area under the basal section of the barnacle. With this coating, the growth of the barnacle was such that permanent deformation of the coating had occurred, which resulted in the formation of an imprint in the coating, as shown in Fig. 1 and Fig. 2.

Had the barnacle (Fig. 1) settled on the panel immediately following immersion, its maximum possible life would have been 1 yr. This imprint showed at least seventy distinct rings, and if it could be shown that these rings were related to the growth cycle of the barnacle, imprints could provide a high degree of precision in studies of their growth. In Fig. 2, the imprints of two different barnacles are apparent, and the interference between each, is visible. Imprints ranging in diameter from 2 mm to about 25 mm, have been recorded. Although the chlorosulphonated polyethylene coatings were permanently deformed, no penetration of the coating had occurred.

The black, two-component, air-cured, chlorosulphonated polyethylene coating system, which was fully cured after 10d, had a hardness of 60 IRHD, an average thickness of 0.24 mm, an elongation at break of 175%, a polymer content of 58%, by weight, and a reinforcing filler content of 35%, by weight. The coating and the timber panel, remained in excellent condition following immersion in seawater for 3 yr. Some of the timber panels were impregnated with an organotin toxicant prior to coating; this did not affect the ability of the barnacle to record its imprint on the coating.

In physically removing the barnacles from the panels some of the basal sections remained firmly attached to the coating. This calcareous material was dissolved away using dilute hydrochloric acid, and the imprint then washed with water followed by acetone. The imprints shown in Fig. 1 and 2 were revealed using this technique. Low-angle, side illumination and standard photographic equipment and techniques were used to record the imprints.

Using an enlarged photographic print of Fig. 1, the detailed pattern of the imprint (1 yr specimen) was determined, and is shown in Fig. 3. The area of every fourth ring was determined from the contour diagram (Fig. 3) and plotted against the number of rings, as shown in Fig. 4. Providing the imprint pattern is associated with the growth of the barnacle, the curve gives an indication of rate of growth. If information on the time of settlement was available, it should be possible to correlate this rate of growth with specific environmental factors, such as those reported by Barnes[3].

Measurement of the profile of the imprint shown in Fig. 1, were made along the axis AB (Fig. 3) using a "Talysurf" instrument, having a pick-up with a stylus of 0.00004 mm tip radius. Maximum distortion of the rubber coating occurred in the region between the initial growth point (I) and A (Fig. 3), where the amplitude of the distortion (at G), was found to be 0.12 mm (equivalent to 50% of the total coating thickness). The distortion of the coating between contours 41 and 53 was approximately 0.05 mm, and between contours 65 and 73 was usually less than 0.01 mm. This type of profile, together with the barnacle adhesive, is probably important in determining the degree of attachment to the particular substrate.

We believe the observation of the ability of the barnacle to record imprints on a chlorosulphonated polyethylene coating, could be of interest to marine biologists. Controlled experiments will be necessary to determine whether the pattern of the imprint is associated with the growth cycle. In this event, factors such as water temperature, weather and tidal conditions, seawater composition and nutrient content, and the effect of toxicants incorporated into the rubber, could be studied in the actual environment using this technique. The physical properties of a range of synthetic rubbers need to be further investigated in order to define the specific factors required for the optimum recording of imprints.

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Department of Supply,
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P. DUNN

GEORGE F. SANSOM

1. Ferguson Wood, E.J. and Allen, F.E. 1958. Common marine fouling organisms of Australian waters. Published by Department of Navy, Navy Office, Melbourne.

2. Ketchum, B.H. and Redfield, A.C. (Ed.). 1952. Marine fouling and its prevention. Contribution No. 580. Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, for Bureau of Ships, Navy Department. US Naval Institute, Annapolis, Maryland, USA. Chap. 9, p. 118.

3. Barnes, H. and Barnes, M. 1954. OIKOS, 5, No. 1, 63.

Fig. 1. Imprint of a barnacle on a chlorosulphonated polyethylene coated timber panel, that had been immersed for 1 yr in tropical waters off the coast in North Queensland, Australia. The average basal diameter of the barnacle was 18 mm.

Fig. 2. Imprints of two barnacles of different species, on a coating immersed for 3 yr. The average basal diameters of the barnacles were 10 mm and 18 mm. The imprint of the large barnacle was revealed by removal of the basal remains using hydrochloric acid.

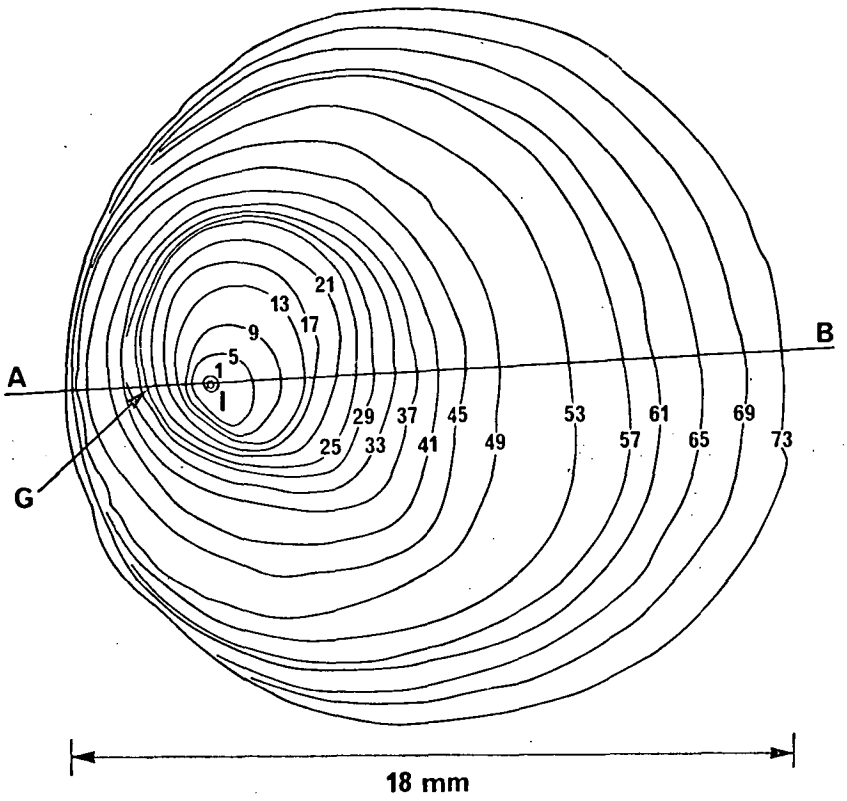

Fig. 3. Contours of the barnacle imprint shown in Fig. 1. The contours represent every fourth ring, numbered from the initial growth point of the barnacle.

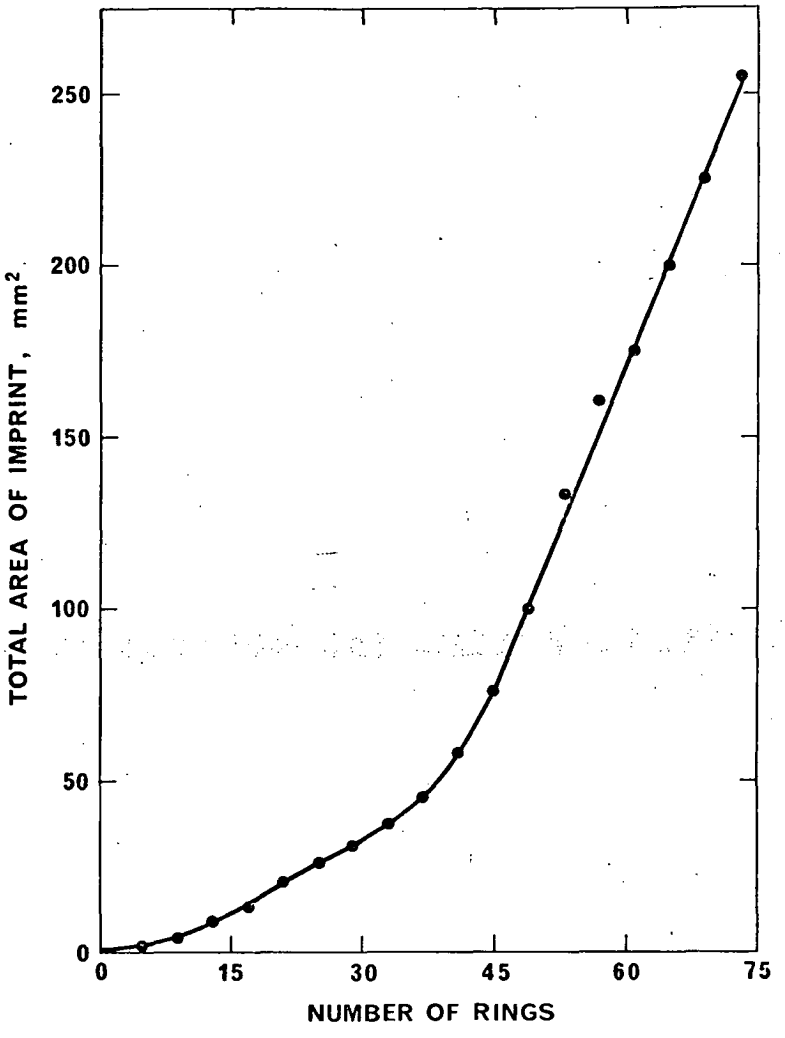

Fig. 4. Basal areas of the barnacle shown in Fig. 1, plotted against a number of rings. The areas were obtained from the contour diagram shown in Fig. 3.

APPENDIX 22b

COMPOSITION OF CHLOROSULPHONATED POLYETHYLENE COATING MATERIAL

General details of the chlorosulphonated polyethylene coating material used to record growth imprints, are:-

The coating consisted of a two-part, lead cured system. Part A contained Hypalon 40, chlorosulphonated polyethylene (Du Pont), clay and titanium dioxide fillers, selected additives and an aromatic hydrocarbon solvent. Part B (accelerator) contained tribasic lead maleate, epoxy resin, antioxidants, accelerators and a mixed solvent system based on toluene. Parts A and B when mixed in the ratio of 16:1, by volume, had a solids content of 44%, by weight.

Following the application of two coats of standard primer, nine layers of coating material were applied and allowed to air dry. The thickness of the final coating was 0.24 mm.

Precise details (Commercial-in-Confidence) of the coating have been recorded in an Addendum to MRL Report 498 (1972) (Ref 184), page 5, para 8, under the heading, Chlorosulphonated Polyethylene - Material Code "H".

APPENDIX 23 FIRE HAZARDS OF ORGANIC MATERIALS

23a The Combustion of Organic Polymeric Materials. Smoke Generation
J.R. BROWN and P. DUNN
Report 560. Defence Standards Laboratories, Department of Supply, Melbourne, Australia. 23.2

23b The Combustion of Organic Polymeric Materials. Evaluation of Flammability by the Oxygen Index Method.
J.R. BROWN and P. DUNN
Report 561. Defence Standards Laboratories, Department of Supply, Melbourne, Australia. 23.3

23c Fire Hazards of Organic Materials - Small Scale Assessment of Flammability and Smoke Generation.
J.R. BROWN and P. DUNN
Fire and Materials, 1, 2 (1976). 23.4 - 23.10

DEPARTMENT OF SUPPLY

AUSTRALIAN DEFENCE SCIENTIFIC SERVICE

DEFENCE STANDARDS LABORATORIES

MARIBYRNONG VICTORIA

REPORT 560

THE COMBUSTION OF ORGANIC POLYMERIC MATERIALS.

SMOKE GENERATION

J. R. Brown and P. Dunn

June 1973

POSTAL ADDRESS: Chief Superintendent, Defence Standards Laboratories,
P.O. Box 50, Ascot Vale, Victoria 3032, Australia.

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DEPARTMENT OF SUPPLY

AUSTRALIAN DEFENCE SCIENTIFIC SERVICE

DEFENCE STANDARDS LABORATORIES

MARIBYRNONG VICTORIA

REPORT 561

THE COMBUSTION OF ORGANIC POLYMERIC MATERIALS – EVALUATION OF FLAMMABILITY BY THE OXYGEN INDEX METHOD

J. R. Brown and P. Dunn

June 1973

POSTAL ADDRESS: Chief Superintendent, Defence Standards Laboratories,
P.O. Box 50, Ascot Vale, Victoria 3032, Australia.

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Fire and Materials 1976, 1, 2 to 8

Fire Hazards of Organic Materials—Small Scale Assessment of Flammability and Smoke Generation

J. R. BROWN and P. DUNN
Australian Defence Scientific Service, Materials Research Laboratories, Department of Defence, Melbourne 3032, Victoria, Australia

(*Received 29 October 1975; accepted 8 December 1975*)

Abstract—The flammability and smoke generation properties of a number of organic materials used in ships, including laminated materials, rigid and flexible cellular polymers, cable insulating materials and adhesives, have been evaluated. The relative flammabilities were determined by the limiting oxygen index method that gives convenient, reproducible, numerical ratings of materials. Smoke generation was assessed photometrically by measuring light attenuation under standard conditions and is reported in terms of the total amount of smoke generated, as well as the times for the smoke density to reach an arbitrary 'critical' level and the maximum value. Materials with low flammability and low smoke generation characteristics have been identified, as well as those that would be hazardous in the event of a fire.

Introduction

IN RECENT years there has been a marked increase in the use of polymeric materials in industrial, military and consumer applications. Because of the danger to life and property by the onset of a major conflagration, all aspects of the behaviour of these materials towards fire need to be understood. In a fire, major hazards can result from the combustion of organic materials including rapid flame spread, heat and smoke generation, oxygen depletion and the production of superheated gases and toxic and corrosive combustion products. In describing fire hazard properties, it has been customary to cite burning rates determined by a multiplicity of small scale tests[1] that have been developed and are being modified continually. Specimens of various dimensions are ignited and arbitrarily assessed by a number of broad classifications that refer only to the defined conditions and often do not relate to the behaviour of materials in actual fire situations. In addition, some tests show poor sensitivity and reproducibility.

The introduction of the limiting oxygen index (LOI) method[2–4] has provided a simple, reproducible test that has been recognized as particularly suitable for research directed towards enhancing the resistance of polymers to fire and for the quality control of materials.[5–11] This technique has been adopted as a standard by the American Society for Testing and Materials.[12] A recent extension of the method to enable measurements to be made at elevated temperatures[13,14] provides further information on material burning behaviour.

Serious attention is now being given to the measurement of smoke generation from materials in fire situations[15,16] as this is a major factor that affects the ability to escape from burning structures. Although no major regulations concerning smoke generation have been issued, a considerable research effort has been directed towards the reduction of smoke from burning organic materials. Laboratory test methods have been developed for measuring smoke generation, the most widely used being the Rohm and Haas XP2 smoke density test[17,18] and the National Bureau of Standards (NBS) smoke density test.[19,20] Test programmes by ASTM members[18] have led to the adoption of the Rohm and Haas XP2 test as a standard for measuring smoke generation from the combustion of plastics.[21] Additional testing[22] has indicated that the NBS test is useful for evaluating materials such as surface coatings, wall coverings, laminates and carpet materials, as well as solid plastics.[23]

In the present investigation, the fire hazards of a number of polymeric materials used in ships were evaluated in terms of their flammabilities by the LOI method and their smoke generating properties which limit visibility in a fire situation, using a Rohm and Haas XP2 Chamber.

Experimental

MATERIALS

The types of materials evaluated were: laminated materials, rigid and flexible cellular polymers, cable insulating materials and adhesives.

The names of the materials studied are given in the first column of Tables 1–4.

ASSESSMENT OF FLAMMABILITY AND SMOKE GENERATION

The LOI of each material was determined according to ASTM D 2863-74 using a General Electric flammability index tester. The smoke generation was measured in accordance with ASTM D 2843-70.

TEST SPECIMENS

LOI. Specimen dimensions for material types A and C of ASTM D 2863-74 were used.

oke Generation. All test specimens had the ard dimensions specified in ASTM D 2843-70 t for cellular polymers. The specimen dimensions id and flexible cellular materials were increased to ±0.3 mm by 25.4±0.3 mm by 25.4±0.3 mm. specimens were conditioned to 23±2°C and % relative humidity for two days prior to testing.

Results and discussion

KE DENSITY DATA

a developing fire, the rate of smoke generation is of derable interest. In a fully developed fire, concern to the effects of smoke in adjacent structures and sures so that the total amount of smoke produced nes the important factor. Smoke measurements us presented in terms of the time for smoke from ng materials to reach specific densities and the num smoke density reached.

smoke density measurements using a parallel of light, the law of extinction (Beer's Law) is given e relationship

$$F = F_0 e^{-\sigma l}$$

F is the transmitted flux, F_0 is the incident flux, he attenuation coefficient and l is the light path a. Optical density, defined as

$$D = \log_{10}(F_0/F)$$

ore convenient measure of light attenuation, as is ecific optical density D_S, which gives the optical y measured over unit path length within a chamber it volume from a specimen of unit surface area. value is defined as

$$D_S = D\frac{V}{Al} = \left(\frac{V}{Al}\right)\log_{10}(F_0/F)$$

A is the surface area of the material generating oke and V is the volume of the chamber. Measure- expressed in terms of the dimensionless D_S have dvantage of representing ideally a smoke density endent of chamber volume, specimen size or photometer path length. There are, however, limitations when comparing specific optical densities calculated from other chamber volumes, surface areas and photometric systems.[20]

For the Rohm and Haas XP2 chamber, in which $V=0.071$ m^3 and $l=0.305$ m, the nominal geometric factors (V/Al) for specimens 25.4 mm by 25.4 mm and thickness 6.4 mm and 25.4 mm are 240 and 120, respectively.

A typical plot of percentage light absorption as a function of time is shown in Fig. 1. The maximum specific optical density, D_m, corresponds to maximum light absorption. The recorded time periods include (a) the time taken for D_S to reach a value of 16 (T_1) and (b) the time taken for the smoke density to reach 90% of its maximum value (T_2). The latter time period can be determined more precisely than the time taken to reach the maximum smoke density. The value for D_S of 16 is an arbitrary figure of smoke density. It has been found experimentally[16] that this represents the value corresponding to the condition in a smoke-filled room at which visibility became so reduced as to hinder escape. For the Rohm and Haas XP2 chamber, the values of D_S equal to 16 for specimens of sizes 25.4 mm by 25.4 mm and thickness 6.5 mm and 25.4 mm correspond to light absorptions of 14.2% and 26.4%, respectively.

The smoke density rating is defined as the area beneath the light absorption–time curve, expressed as a percentage of the area 0–4 min, 0–100% light absorption. This rating represents the total amount of smoke in the chamber for the four minute time interval of the test. Smoke density ratings of materials for which the light absorption reaches 100% must be regarded as minimum values, as smoke may continue to accumulate after the light transmission has been reduced to zero. The smoke density rating does not differentiate between materials in which a rapid smoke generation occurs and those in which smoke generation is slower. This is illustrated by the variation between the T_1 values and the corresponding smoke density ratings of the materials in Tables 1–4. The smoke generation data represent the averaged data from six test specimens and errors are within ±5%. Repeatability depends on the type of material, and in general, slow burning materials show a larger scatter in results.

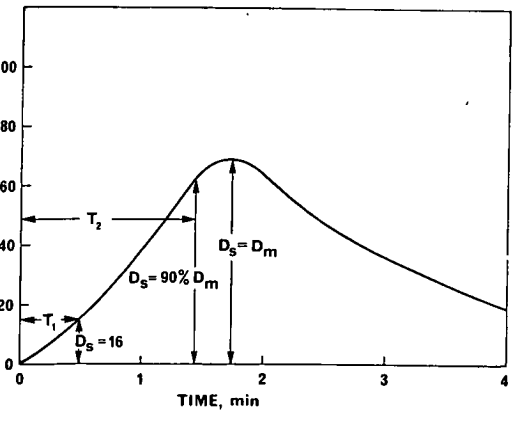


FIG. 1. Typical light absorption vs time plot.

LAMINATED MATERIALS

Two types of laminated materials were evaluated, decorative melamine paper laminates and glass fibre laminates. Standard grades of melamine paper laminate have relatively low flammabilities and generate small amounts of smoke at a slow rate as shown in Table 1 and Fig. 2. Fire-retarded melamine paper laminates have very high LOI values (35–60). Those materials with LOI values greater than 50 burned erratically at oxygen concentrations greater than their LOI values and also exhibited the phenomenon of afterglow. The values given are those below which afterglow and flaming

TABLE 1. Smoke generation and flammability data for laminated materials

Material	Maximum light absorption (%)	Maximum specific optical density (D_m)	Smoke density rating (%)	Time (s) T_1	Time (s) T_2	LOI
MPL[a] (1.1)	4	4	3	—	200	26.0
MPL (1.2)	31	39	10	170	225	29.5
MPL-FR[b] (1.3)	59	93	26	90	195	36.8
MPL-FR (1.4)	36	47	17	105	195	58.2
MPL-FR (1.5)	87	213	62	34	135	51.0
GRP[c] (1.6)	99	480	88	12	42	19.8
GRP-FR (1.7)	100	∞	92	7	30	31.4

[a] Melamine paper laminate.
[b] Fire retardant grade.
[c] Glass reinforced polyester.

combustion are not supported. The fire-retarded grades generated appreciably more smoke than the untreated materials.

Table 1 shows the superior flame resistance of a fire-retarded polyester glass fibre laminate compared with a standard grade. Table 1 and Fig. 2 also show that for both fire-retarded and untreated materials, smoke generation is rapid and extensive. As this type of material is widely used in the interior of ships, the need exists for the development of fire resistant glass fibre reinforced polyester and epoxy laminates that generate less smoke on combustion.

RIGID AND FLEXIBLE CELLULAR POLYMERS

The fire hazard associated with the utilization of cellular polymers as insulating materials in ships is of particular interest. Smoke density data and LOI values for several types of cellular polymers are given in Table 2 and Fig. 3. LOI ratings of fire-retarded rigid polyurethane foam are in the range 22–23, compared with a value of about 18 which is typical for rigid polyurethanes containing no fire retardants. Polyisocyanurate foams are more thermally stable than polyurethane;[24,25] our results show that the LOI is markedly greater than those of rigid polyurethane foams.

Polyester-based urethane flexible foams are less flammable than the polyether-based urethane flexible foams. This is attributed to a higher yield of carbon dioxide in the thermal decomposition products of the polyester-based material.

Rigid expanded poly(vinyl chloride) materials have higher LOI values than rigid polyurethane foams. This property, together with their high structural integrity, makes them very useful materials. A major disadvantage is that dehydrochlorination is one of the principal thermal decomposition reactions and this results in the liberation of corrosive hydrogen chloride on burning. Flexible expanded poly(vinyl chloride) has a relatively low flammability (LOI, 25–27), which is influenced by the type of plasticizer present.

The most significant aspect of the development of smoke from the combustion of expanded polymeric materials is that the maximum smoke density occurs in a

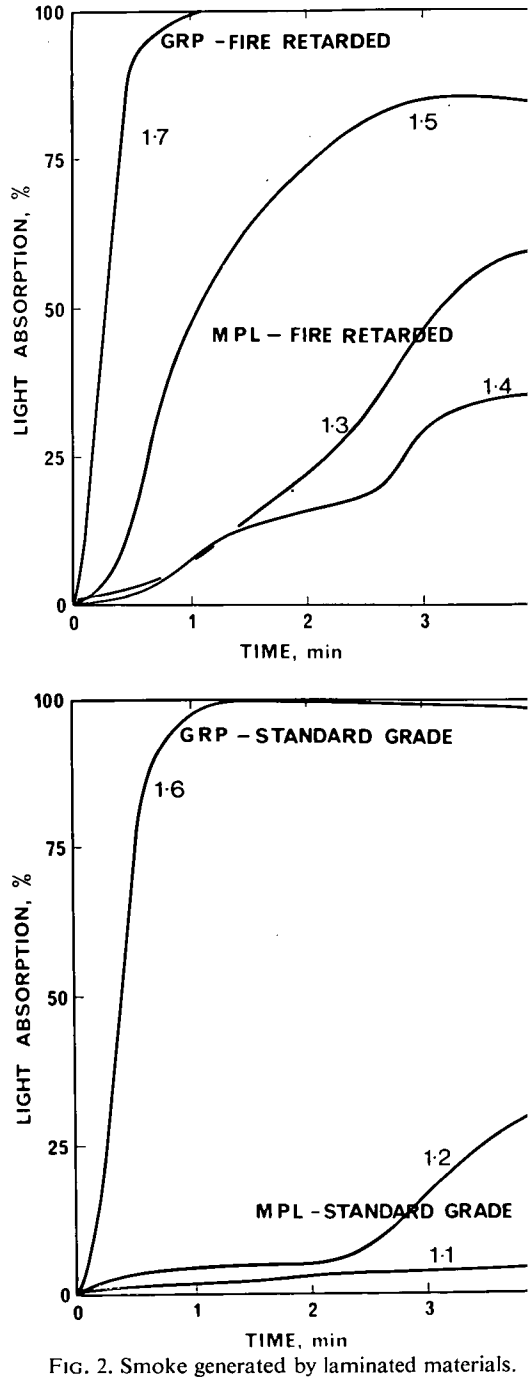


FIG. 2. Smoke generated by laminated materials.

TABLE 2. Smoke generation and flammability data for rigid and flexible cellular polymers

Material	Maximum light absorption (%)	Maximum specific optical density (D_m)	Smoke density rating (%)	Time (s) T_1	Time (s) T_2	LOI
Rigid polyurethane[a] (2.1)	89	115	62	6	15	21.9
Rigid polyurethane[a] (2.2)	75	72	48	7	15	22.9
Rigid polyurethane[a] (2.3)	88	110	58	5	12	23.3
Rigid polyisocyanurate (2.4)	30	19	21	45	47	30.8
Flexible polyurethane[b] (2.5)	9	5	5	—	6	16.7
Flexible polyurethane[c] (2.6)	12	7	7	—	7	20.5
Flexible polyurethane[d] (2.7)	26	16	16	12	11	22.3
Flexible polyurethane[d] (2.8)	11	6	6	—	6	24.9
Rigid poly(vinyl chloride) (2.9)	99	240	81	6	14	31.8
Rigid poly(vinyl chloride) (2.10)	88	110	43	6	16	26.3
Rigid poly(vinyl chloride) (2.11)	88	110	68	8	26	34.6
Polystyrene[a] (2.12)	52	38	26	6	8	29.3
Flexible poly(vinyl chloride) (2.13)	88	110	71	8	26	26.9
Flexible poly(vinyl chloride) (2.14)	93	139	74	8	39	25.6
Poly(vinyl chloride) polyacrylonitrile (2.15)	95	156	77	6	20	24.3
Expanded rubber latex foam (2.16)	100	∞	94	4	24	17.3

[a] SE grade (self-extinguishing).
[b] Ether type.
[c] Ester type.
[d] Ether type and containing a fire retardant.

t time (Fig. 3). Polyurethane foams are rendered extinguishing' by various methods involving the rporation of reactive and non-reactive fire retard-[26–29] The term 'self-extinguishing' is now widely gnized as misleading and is strongly discouraged by e concerned with the legality of fire terminology. retarded rigid polyurethanes generate a substantial unt of smoke that is influenced by the types of fire dants used. Polyisocyanurate foam generates much smoke and at a slower rate, and retains the advant- of rigid polyurethanes such as low thermal con- vity and low density. Flexible polyurethanes burn lly and the low smoke generation compared with polyurethanes of similar density reflects the rences in chemical composition and structure.

gid poly(vinyl chloride) foams burn slowly but e copious quantities of smoke containing hydrogen ide. The differences in levels of smoke generated by igid poly(vinyl chloride) foams reflect differences in ties of the materials. Flexible poly(vinyl chloride) materials behave in a similar manner, but the amount of smoke generated can be markedly affected by the type of plasticizer used.

Expanded rubber latex foam consisting of 75 parts of natural rubber and 25 parts of styrene+butadiene rubber burns readily in air and generates large quantities of smoke. In a fire situation, this material would present a serious hazard in ships.

Because of their low density, cellular materials may evolve less total smoke than some of the traditional materials used in the same applications, but rapid smoke generation at an early stage in the combustion can be expected. The action of fire retardants in reducing flame-spread can result in increased smoke and the entrainment of small particles of material in the combustion products.

CABLE INSULATING MATERIALS

Table 3 and Fig. 4 illustrate the flammability and smoke generation properties of several cable insulating

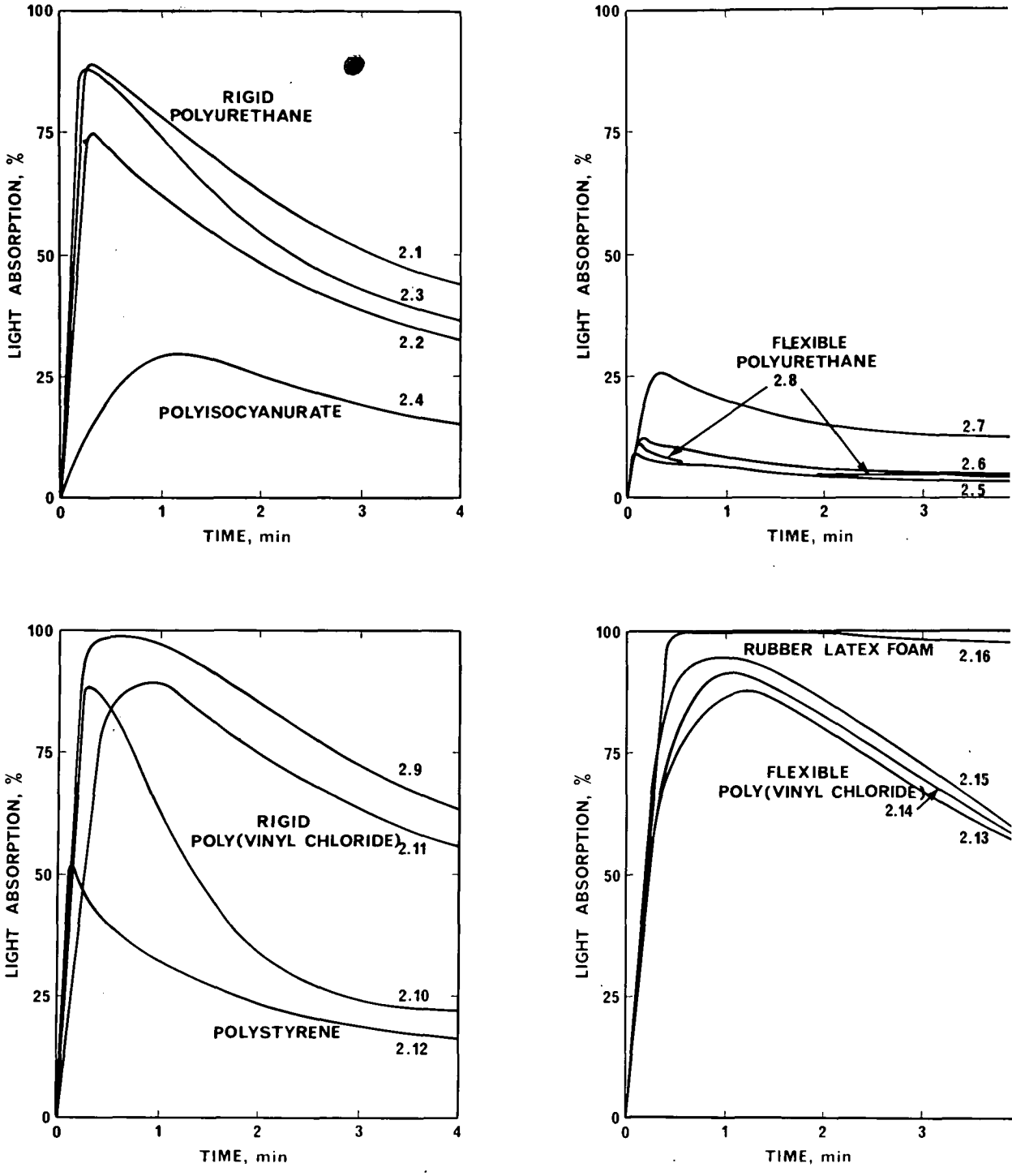
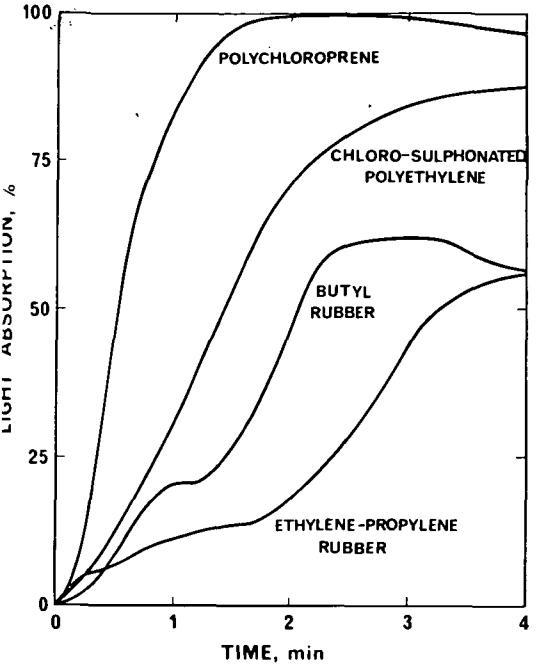


FIG. 3. Smoke generated by rigid and flexible cellular polymers.

TABLE 3. Smoke generation and flammability data for cable insulating materials

Material	Maximum light absorption (%)	Maximum specific optical density (D_m)	Smoke density rating (%)	Time (s)		LOI
				T_1	T_2	
Butyl rubber	62	101	39	42	72	20.1
Ethylene + propylene rubber	56	86	25	74	180	21.0
Polychloroprene	99	480	84	16	72	30.9
Chloro sulphonated polyethylene	88	221	58	35	150	30.9
Polychloroprene	97	365	71	23	114	31.8
Poly(vinyl chloride)	100	∞	94	5	29	25.5
Silicone rubber	50	72	27	65	202	31.2



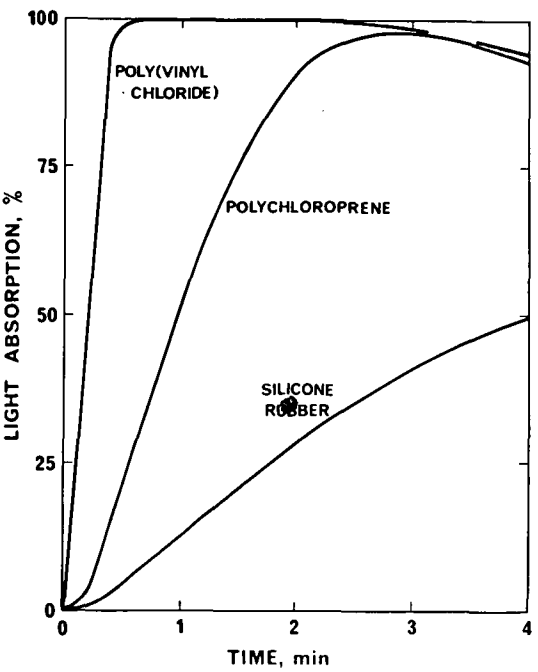
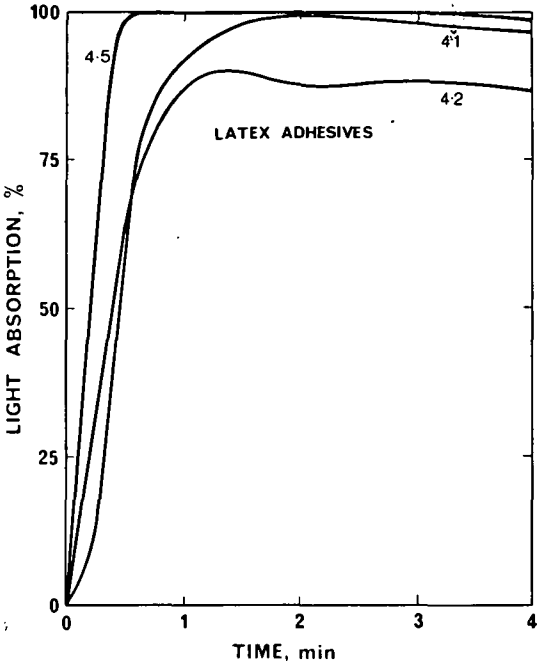


FIG. 4. Smoke generated by cable insulating materials.



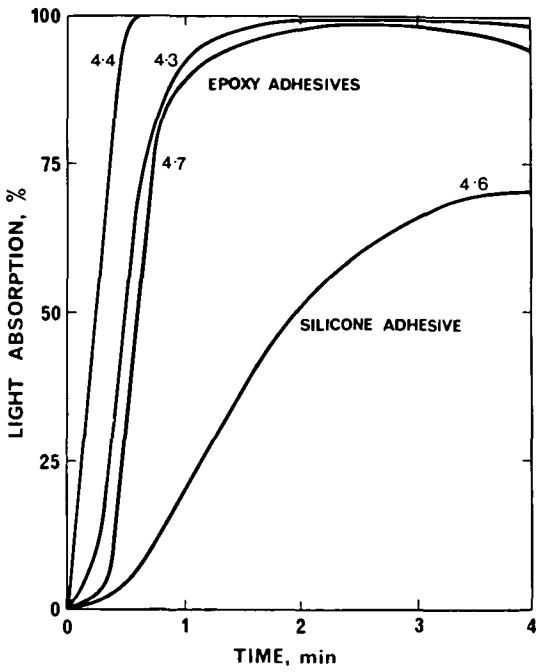


FIG. 5. Smoke generated by adhesive materials.

TABLE 4. Smoke generation and flammability data for adhesive materials

Material	Maximum light absorption (%)	Maximum specific optical density (D_m)	Smoke density rating (%)	Time (s) T_1	Time (s) T_2	LOI
Latex adhesive (4.1)	99	480	86	15	57	21.6
Latex adhesive (4.2)	90	240	80	8	48	19.8
Epoxy adhesive (4.3)	99	480	89	17	49	20.6
Epoxy adhesive (4.4)	100	∞	94	5	27	19.9
Synthetic rubber adhesive (4.5)	100	∞	95	5	25	27.3
Silicone adhesive (4.6)	70	125	43	50	165	24.2
Vinyl epoxy adhesive (4.7)	98	408	82	23	59	23.3

and sheathing materials. Butyl rubber and ethylene+propylene rubber are quite flammable (LOI, 20–22) whereas the polychloroprenes and chlorosulphonated polyethylenes have low flammabilities (LOI $\simeq$ 30) as does silicone rubber. The flammability of poly(vinyl chloride) insulation material lies between these two groups.

Smoke generation data show that the polychloroprenes and poly(vinyl chlorides) evolve more smoke on combustion than do the ethylene+propylene and butyl rubbers. This is in agreement with the general observation that many polymers with low flammability characteristics generate large quantities of smoke on combustion. Chlorosulphonated polyethylene also generates appreciable smoke on combustion, but at a much slower rate than the polychloroprenes. Silicone rubber generates only a small quantity of smoke on burning.

ADHESIVES

The types of adhesives and the corresponding LOI values and smoke generation data are listed in Table 4. Epoxy and latex adhesives burn in an atmosphere of $22 \pm 2\%$ oxygen, and thus have relatively high flammabilities. Smoke generation is substantial, particularly from epoxy material, as shown in Fig. 5. However, because of the small quantities of adhesives normally used, smoke generation from this class of material should not be a major hazard.

Conclusions

Flammability and smoke generation properties of a number of organic materials used in ships have been evaluated in small scale tests and materials that may be a fire hazard have been identified. It is not suggested that the total assessment of the hazards can be made on the basis of these tests alone. They do not assess important factors such as flame-spread rate, ignition temperature and heat production, or the problems associated with corrosive and toxic combustion products. They must be used in association with other tests that measure these properties in order to allow detailed evaluation of materials during combustion.

REFERENCES

1. N. K. Raman, K. A. Scott and W. Taylor, *Rubber and Plastics Research Association of Great Britain Tech. Rev.* 58 (1971).
2. C. P. Fenimore and F. J. Martin, *Combust. Flame* 1 (1966); *Mod. Plast.* **44**, 141 (1966).
3. J. L. Isaacs, *J. Fire Flammability* **1**, 36 (1970).
4. K. B. Goldblum, *SPE J.* **25**, 50 (1969).
5. C. P. Fenimore and G. W. Jones, *Combust. Flame* 1 (1966).
6. J. Di Pietro and H. Stepniczka, *J. Fire Flammability* (1971).
7. A. J. Papa and W. R. Proops, *J. Appl. Polym. Sci.* 16 (1972).
8. W. Batorewicz and K. A. Hughes, *J. Fire Flammability* (1971).
9. J. J. Willard and R. E. Wondra, *Text. Res. J.* **40**, 203 (19
10. G. C. Tesoro and C. H. Meiser, *Text. Res. J.* **40**, 430 (19
11. J. E. Hendrix, J. V. Beninate, G. L. Drake and W. A. R *J. Fire Flammability* **3**, 2 (1972); *Text. Res. J.* **41**, 854 (
12. Standard Method of Test for Flammability of Plastics the Oxygen Index Method. Test Method D 2863-74. Am Society for Testing and Materials, Philadelphia, 1974.
13. J. R. Dunn and R. Novak, Improved Small Scale Te Flammability of Polymers. Paper presented at A Symposium on Measurement and Assessment of Respo Plastics Materials to Fire Exposure, Los Angeles, Calif 1972.
14. A. F. Routley, Central Dockyard Laboratory Report, Portsmouth, U.K., 1973.
15. J. R. Gaskill, *J. Fire Flammability* **1**, 183 (1970).
16. C. J. Hilado, *J. Fire Flammability* **1**, 217 (1970).
17. Rohm and Haas Co., *NFPA Q.* **57**, 276 (1964).
18. F. J. Rarig and A. J. Bartosic, *ASTM S. T. P. 422*, p American Society for Testing and Materials, Philade 1966.
19. D. Gross, J. J. Loftus, T. G. Lee and V. E. Gray, Na Bureau of Standards (U.S.) Report, NA-68-36, 1968.
20. D. Gross, J. J. Loftus and A. F. Robertson, *ASTM S. 422*, p. 166. American Society for Testing and Mat Philadelphia, 1966.
21. Standard Method for Measuring the Density of Smoke the Burning or Decomposition of Plastics. Test M D 2843-70. American Society for Testing and Mat Philadelphia, 1974.
22. T. G. Lee, National Bureau of Standards (U.S.) Tech Note 708, 1971.
23. D. Cross, J. J. Loftus, T. G. Lee and V. E. Gray, Nat Bureau of Standards (U.S.) Building Science Series 18,
24. G. W. Ball, G. A. Haggis, R. Hurd and J. F. Wood, *J. Plast.* **4**, 248 (1968).
25. I. N. Einhorn, J. D. Seader, W. O. Drake, C. M. Mihlfeitl M. D. Kanakia, *Polym. Eng. Sci.* **12**, 167 (1972).
26. A. D. Delman, *J. Macromol. Sci. Rev. Macromol. C* **3**, 281 (1969).
27. M. Sander and E. Sleininger, *J. Macromol. Sci. Rev. Macr Chem.* **2**, 1 (1968).
28. A. J. Papa, *Ind. Eng. Chem. Prod. Res. Dev.* **9**, 478 (197
29. J. W. Lyons, *The Chemistry and Uses of Fire Retard* p. 345. Wiley-Interscience, New York, 1970.

APPENDIX 24 MISCELLANEOUS ACTIVITIES - ORGANIC MATERIALS

24a	Half Section of a Direct Moulded Sole(DMS) Military Boot	24.2
24b	Direct Moulded Soles for Combat Footwear. Part I. Current Production P. DUNN and S.J. HART Report 336. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.	24.3 - 24.5
24c	Rubber and Metal *Austfire* Targets P. DUNN and T. LIGGINS Report 294. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.	24.6 - 24.8
24d	Rubber Plugs for Detonantless Fuzes P. DUNN and T. LIGGINS Technical Note 97. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.	24.9 - 24.10
24e	The Weathering of Polyolefins. P. DUNN and E.J. HILL. Report 421. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.	24.11 - 24.12

Appendix 24a - Half section of a direct moulded sole military boot showing the stainless steel anti-spike insole plate (mag., 0.6).

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REPORT 336

DIRECT MOULDED SOLES (DMS) FOR COMBAT FOOTWEAR
PART 1: CURRENT PRODUCTION

P. Dunn and S. J. Hart

SUMMARY

Direct moulded sole (DMS) combat boots have been manufactured in Australia since September, 1965, and have given excellent service both in Australia and in Vietnam. Details are given of the design, inspection and production of DMS combat boots, especially in regard to the development of the rubber components of the boots. Alternative materials have been evaluated for possible replacement in the suggested formulation, should supply difficulties arise.

No major changes in the rubber formulations of the boots are proposed for current production. Some minor design changes, however, could be introduced to facilitate production and inspection and to improve performance.

"The information contained in this report is mainly based on our own laboratory work employing small-scale equipment, but following generally accepted processing procedures. Manufacturing trials would be necessary to confirm that the results reported could be reproduced using larger-scale equipment".

MARCH, 1969

POSTAL ADDRESS: Chief Superintendent, Defence Standards Laboratories, Box 50, P.O., Ascot Vale, 3032, Victoria.

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TABLE 6 : Effect of plasticizer variation on the properties of the boot sole compounds

FIG. 1 : Current production sample of DMS combat boots

FIG. 2 : Rheographs showing the effect of different PVC resins on the curing characteristics of compounded rubbers

FIG. 3 : Rheographs showing the effect of temperature on the curing characteristics of a compounded rubber

FIG. 4 : Rheograph showing the effect of prewarming temperature on the viscosity of a compounded rubber

FIG. 5 : Rheograph showing the effects of accelerator modifications

FIG. 6 : A typical example of DMS combat boots returned from service in Vietnam

A. Complete boot showing condition of the uppers

B. Boot sole showing condition of the tread

FIG. 7 : Rheograph reference curve

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REPORT 294

RUBBER AND METAL "AUSTFIRE" TARGETS

P. DUNN and T. LIGGINS

SUMMARY

A highly-filled, insulating, polychloroprene ("neoprene") rubber has been developed for bonding onto a perforated metal backing. This metal and rubber target is used for improved hit counting on an electromechanical target range known as "Austfire".

The hit counting system depends on the amplification and recording of electrical pulses generated by bullet hits on a rubber covered target. The mechanical properties of the rubber are superior to, and the electrical properties similar to, those of a commercial floor tile rubber which had been shown to develop a pulse of acceptable amplitude.

A specification has been issued by Department of the Army to enable finished targets to be produced by industry.

APRIL, 1967

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TABLE 10. Physical Properties of Target Facing Rubber.

APPENDIX. Details of Proprietary Materials.

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TECHNICAL NOTE 97

RUBBER PLUGS FOR DETONANTLESS FUZES

P. DUNN and T. LIGGINS

SUMMARY

Soft rubber plugs based on a natural rubber-polychloroprene (Neoprene) rubber blend have been developed for use in detonantless fuzes. Formulation and production modifications have enabled components to be produced by normal production techniques.

During the last few years over 25,000 rubber plugs of varying designs have been produced in the laboratory and by industry for use in detonantless fuzes.

MAY, 1967

POSTAL ADDRESS Chief Superintendent, Defence Standards Laboratories, Box 50, P.O., Ascot Vale, W.2, Victoria.

PRINTED BY DEPARTMENT OF SUPPLY, CENTRAL DRAWING OFFICE, MARIBYRNONG, W.3.

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DEPARTMENT OF SUPPLY
AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
DEFENCE STANDARDS LABORATORIES

REPORT 421

THE WEATHERING OF POLYOLEFINS

P. DUNN and E. J. HILL

SUMMARY

A series of five types of polyolefins has been exposed for four years at four outdoor sites in Australia with widely differing climatic conditions. Injection moulded plaques and tensile test specimens were used, and mechanical and electrical properties determined, both before and after exposure.

A total of twenty-three (23) materials was exposed, consisting of six (6) polypropylenes, five (5) high-density polyethylenes, five (5) low-density polyethylenes, four (4) high-density — low-density polyethylene blends and three (3) poly(ethylene-ethyl acrylate) copolymers. Unpigmented (natural) materials as well as materials pigmented with coloured inorganic pigments or carbon black, were exposed. Details are given of the effect of weathering on the polyolefins, and recommendations made concerning the use of these materials in outdoor applications.

MARCH, 1971

POSTAL ADDRESS: Chief Superintendent, Defence Standards Laboratories, Box 50, P.O., Ascot Vale, Victoria, 3032.

PRINTED BY DEPARTMENT OF SUPPLY, CENTRAL DRAWING OFFICE, MARIBYRNONG, VICTORIA 3032

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APPENDIX 25 RADIOACTIVE ISOTOPES IN ANIMAL THYROIDS

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Metropolitan Forecast
Mainly Fine

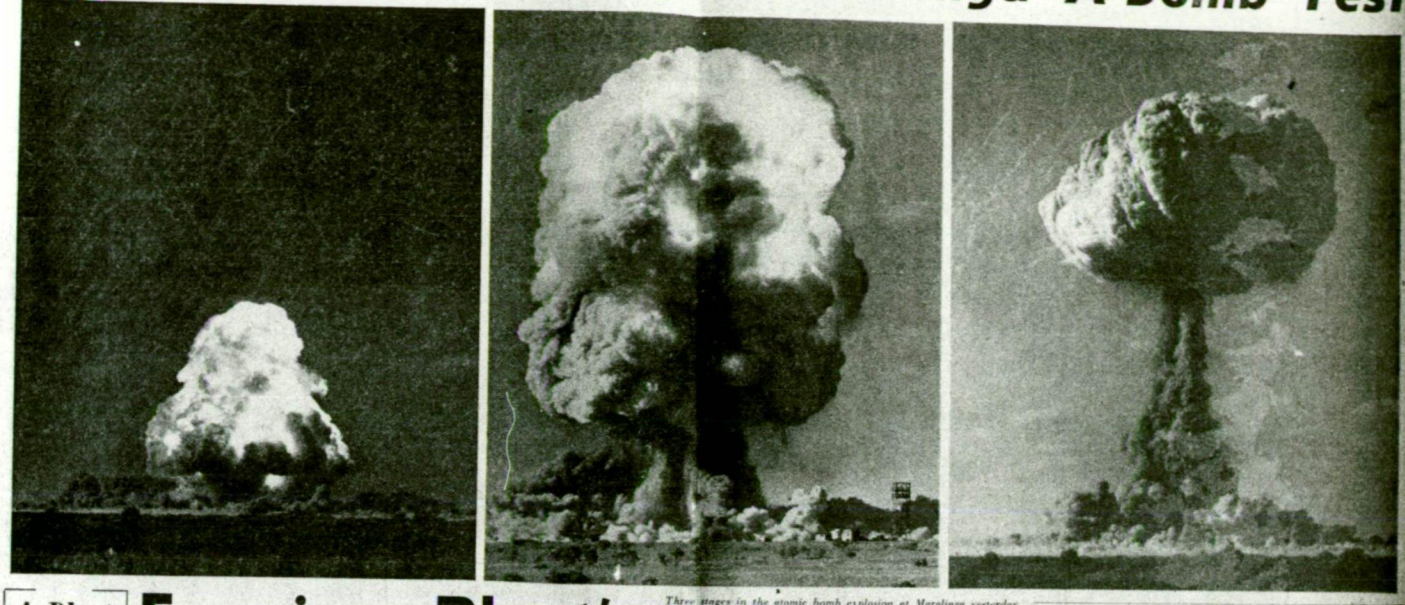
Yesterday's Temperatures
Min., 51.9; max., 61.8.

The Advertiser

WITH WHICH IS INCORPORATED "THE REGISTER."

Vol. 99, No. 30,562 — Adelaide, South Australia, Friday, September 28, 1956 — 26 PAGES—Price 4d.

Three Stages In Penney's Maralinga A-Bomb Test



Three stages in the atomic bomb explosion at Maralinga yesterday afternoon showing (from left):—
1—The nucleus of the blast showing the crisscross pattern left by smoke rockets, fired simultaneously with the detonation of the bomb to permit visual recording of shock waves.
2—The mushroom forming just after the explosion. A test tower can be seen at right and at its foot are steel framed buildings in the target area, some already collapsing under the shock of the blast and others still standing.
3—The bomb cloud extending far into the sky.

A-Blast 'To Plan'

CANBERRA, Sept. 27.

The atomic weapon explosion at Maralinga today, "went according to plan."

This was announced in the House of Representatives today by the Minister for Supply (Mr. Beale).

Mr. Beale said the test's director Sir William Penney had advised that everything went according to plan and prediction and to the entire satisfaction of the Australian Safety Committee and himself.

The atomic cloud behaviour was as forecast and in accord with the requirements of the safety committee, he said.

All precautions to safeguard personnel at the range had been fully enforced, and tracking and checking of the cloud as it dispersed and decayed were taking the normal course.

"Harmless"

Mr. Beale said there might be some slight rise in radio-activity in some areas of Australia but in all cases it would be at quite a harmless level.

He warned that no importance should be attached to Geiger counter readings from fall-out following after the test.

The Geiger counter was a very sensitive instrument, and its readings should only be considered when taken by scientists who used other instruments.

A luminous dialled wrist watch could give a Geiger counter reading of 20,000 counts a minute, which although sounding high, was not harmful.

Mr. Beale said that although in the next few days some aircraft might be delayed or diverted, it did not imply danger. It was just a case of avoiding unnecessary exposure to any radio-activity.

He promised that, in a few days, he would make a statement on how the light particles had dispersed.

"Top Standard"

The Premier (Mr. Playford) said in the Assembly yesterday before the explosion—that "the highest standard of safety in the world" was being applied at Maralinga.

He was replying to Mr. Noon (Ind.).

The Commonwealth Government was taking great care to ensure that there was no likelihood of radio-active fall-out in settled areas, Mr. Playford said.

Because of the uncertainty of the Maralinga project, it would be impracticable to move all cattle to another site, Mr. Playford said.

PERTH, Sept. 27.—There was urgent need for the WA Government to help natives in the Laverton-Warburton Range area because the Maralinga tests were interfering with their way of life, Mr. William Grayden (Ind.-Lib.) said in the Legislative Assembly last night.

He was moving for a select committee to enquire into the welfare of natives in this area.

Evening Blast's Havoc In Desert

From MAX FATCHEN

MARALINGA, September 27.

After 15 nerve-racking days of postponement, Britain's sixth atomic weapon was exploded successfully at Maralinga at 5 p.m today.

The fiery mushroom cloud which followed the explosion of the bomb from a tower surged over the proving grounds before the biggest audience ever to watch a British test.

Towards sunset, a plane reconnaissance by pressmen revealed grim havoc.

There was a grey scar half-a-mile across where the tower had been vaporised.

Much of the target response area, containing buildings, materials and tanks, was ablaze in the evening light.

The dramatic switch to an early evening explosion—the first in a British atomic test—was made to seize favorable weather.

The roar of the explosion hit the Press party, seven miles away, about 12 seconds after the burst.

The correspondent's felt the sudden heat of the flash on their necks as they faced away from it.

A single violent thump reached us 32 seconds after the blast, but surprisingly, we felt no shock waves when taken by scientists who used other instruments.

MOVED IN

Several minutes later, we learned that scientists, wearing protective clothing, had moved into the dangerously radio-active area.

Almost eight minutes after the blast, twin vapor trails of Canberra jet bombers flew into the fast-climbing atomic cloud, which was still connected to the distant test site by a long crossed trail of dust and vapor.

The cloud was a perfect mushroom—on an enormous brown stalk. It climbed into the evening air.

The mushroom took on appearance of a lenormous powder puff, its top pure white, its base flecked with brown.

Fifteen hundred scientists, servicemen, observers and Press people from Britain, Canada, Australia, the US and NZ saw the long-awaited tower burn out in the afternoon desert sky ablaze.

Above five or six miles from the blast were 200 servicemen-the first military getting their first taste of atomic warfare.

The absence of a big shock wave at the Press site seemed to point to the fact that Britain's atomic chief Sir William Penney, and scientists were making bombs of an incredibly smaller critical mass.

The burst came after half an hour of almost unbearable tension.

Dawn was the blast-time first scientists, wearing protective clothing, moved in to clear the dangerous radio-active zone and recover cameras and films.

JETS BUSY

Canberra jet bombers began tracking the atomic cloud at 9 o'clock after the blast, but surprisingly, we felt no shock waves.

Within 20 minutes of the blast, the roads to the smoking target area were busy with convoys of yellow painted vehicles, which will work in contaminated areas.

The unwieldy white mobile health control caravans with gaudy white chimneys rolled forward to take their place behind bounden marking behind genius radio-activity.

Drivers clad in white protective clothing gave the "thumbs up" sign.

The afternoon burst meant a shorter daylight period for early out-posting activities, but the scientists will carry on through the night.

DESERT FIRE

Towards sunset, a flight at 500 ft, two miles south of the bomb area revealed the havoc of the explosion.

Beyond the huge grey scar past the inner area, for another half-mile, the whole countryside was as if by a giant broom, leaving the sand flat and brown desert.

Much of the target response area of tanks, buildings and materials was ablaze.

Two of six aircraft on the ground in the target area had been flung on their backs by the force of the blast.

Buildings about a mile and a half from the bomb had great jagged holes blasted in them. Other buildings were demolished.

• *U.N. Brands Israel As Aggressor, page 6.*

Dust were strained to undercarriages within two miles away.

The Director of Civil Defence in NSW (Maj.-Gen. Ivan Dougherty), who saw the blast, said "This is afearsome thing. It is important to push ahead and organise civil defence."

Wind shifts cancelled the two previous tests—the last Friday morning (40 minutes before firing) and Wednesday morning of this week (only 15 minutes).

After the explosion, the mushroom cloud gradually faded into a cloud which looked like an ordinary cloud moving at a great height under the push of high-level winds.

Some particles from this cloud will gradually float to earth, and some will eventually be brought down by rain.

But the amount of radio-active dust deposited will be detectable by suitable instruments, and are too small to be of any danger to health or risk to stock or property.

Map showing the Maralinga atom bomb test site in relation to surrounding areas.

Shock Check By Seismographs

A seismologist stationed at Cook said the sound of the atomic explosion was heard between 12 and 13 minutes after the blast had been sent.

The seismologist is Mr. R. A. Bolt, who is Lecturer in Geophysics at the Australian National University.

He said he was one of a party of six seismologists stationed at various points along the East-West railway line with seismographs to record shock waves in the earth's crust.

Mr. Bolt said the flash and the mushroom cloud and the explosion could be seen from the scene of the explosion.

"Our object is to pick up waves travel it is through the earth's crust and learn something of the crustal properties of Australia," Mr. Bolt said.

"Actually this explosion corresponds to a rather small earthquake.

"Shock waves from a fair - sized earthquake would be recorded several thousand miles away, but 60 miles would be about the limit for this atomic bomb."

Mr Bolt said independent studies also were being carried out by officers of the Commonwealth Bureau of Mineral Resources.

Seismographs had been set up at Cook, Forrest, Longreach, Rawlinson, Tennant Creek and Kalgoorlie.

It was hoped to record shock waves at Kalgoorlie which was 600 miles from the scene of the explosion.

Our object is to pick up waves travel it is through the earth's crust and learn something of the crustal properties of Australia," Mr. Bolt said.

"Actually this explosion corresponds to a rather small earthquake.

"Shock waves from a fair - sized earthquake would be recorded several thousand miles away, but 60 miles would be about the limit for this atomic bomb."

Mr Bolt said independent studies also were being carried out by officers of the Commonwealth Bureau of Mineral Resources.

Heard Over Big Area Of N.W.

People living hundreds of miles away from Maralinga, in the north-west of the State, said yesterday that they had heard the sound of the atomic explosion.

Many reported that they had heard several explosions in rapid succession.

This was due to a "skip" effect of the sound travelling through the atmosphere, it was explained last night.

The sound of the explosion was heard more than 200 miles away at PIMBA, and people Byling at PENONG, 170 miles SSE of Maralinga, reported that the vibration caused windows and doors to rattle.

RATTLED

The Penong reports said the explosion rattled windows at about 5.10 p.m.

The flash and the mushroom cloud were seen by observers at EUCLA, at BARTON and COOK, more than 70 miles SE and SW respectively from the scene of the explosion.

Observers at Cook said the sound of the explosion reached them between 12 and 13 minutes after they had seen the flash.

The roadmaster at Cook (Mr. C. Copeman) said he heard three distinct blasts.

The report from Penong also said three distinct explosions were heard.

Mrs. P. Wood, wife of the officer in charge of Penong radio station, said there were two minor explosions followed by a loud one.

Other reports from Penong said the explosions made chairs jump off the floor and the ground vibrate.

A spokesman for the BOOKOOYOOKA Mission, 100 miles S-SE of Maralinga, said the explosion was heard and was followed by a loud rumble.

SHOOK HOME

At KINGOONYA, about 200 miles from Maralinga, Mr. A. Bell said the explosion, which sounded like a clap of thunder, rattled shutters and made the house tremble.

Mr. J. W. Bonner, living down in Kingoonya Cemetery Road, said he heard a loud explosion at about 5.10 p.m.

At 5.30 p.m. Mr. Bonner heard another explosion followed by a similar one about 10 minutes later.

"CANNON-LIKE"

Mr. [illegible] of NUNDROO Homestead, 100 miles south of Maralinga, heard four "cannon-like" explosions at 5.10 p.m.

Mr. Stott said the explosions all occurred within about five seconds, and each was louder than the previous one.

They caused the windows of the homestead to vibrate.

The wind was blowing from the south-east at the time.

The sound of the explosion carried more than 100 miles to PIMBA, where it was heard as a low rumble, but at WIRRAMINNA, 40 miles closer to Maralinga, two distinct reports were distinguished.

BASE TOLD

Soon after the explosion people within a 200-mile radius of Maralinga were reporting their impressions of the bomb to the Flying Doctor base at CEDUNA

Most heard two or three "booms" and felt shock waves, and one man saw the effects of the bomb.

The assistant radio operator at the base, 18-year-old Miss Betty Lowe, said last night she heard a bang like a shot of gelignite from "off fairly close" and felt a shock in her legs "like a lift when it pulls up suddenly."

200 MILES

At about 5.15 p.m. Mr. W. Stretton, who lives at 35 miles south of COOBER PEDY — and about 200 miles NE of Maralinga—had called her on the radio and reported hearing an explosion. He told them another about 11 minutes later, and feeling shock waves.

Later he had reported seeing "over hundreds of square miles of countryside around Lake Aterrondrinka, thousands of these deadly snakes appeared.

During the past few days numerous bus loads of visitors have arrived at a local airfield to watch Mr. L. V. Higgins, said yesterday that he had seen hundreds of snakes basking in the sun and bushes.

He added that he and Constables R. E. Arney had killed five snakes in about 30 seconds.

Nurrung people had shot hundreds in the past few days and one local man had killed 150 in an afternoon.

At Marrie Bridge and neighbouring swamp settlements people are being

HOLFE'S SCHNAPPS
With Lemon make a soothing nightcap. (Advt.)

MINISTRY TO BE CHANGED

From Our Staff Representative

CANBERRA, September 27.

The Prime Minister (Mr. Menzies) announced today that "within the next few days" he would be considering changes in the Federal Ministry.

The changes have been made necessary by the transfer of the former Attorney-General (Senator Spicer) to the Arbitration Court bench and the impending nomination of the Minister for Defence Production (Sir Percy Harrison) to become High Commissioner in London.

One of the main points of interest centres on the future of the new Liberal Party deputy leader (Mr. Holt), who has been appointed one of the Government in the House of Representatives.

Busy Post

The leadership post is a particularly busy one during Parliamentary sittings, and Mr. Holt is already loaded with two heavy portfolios—Labor and Immigration.

It is said that some housebuilders claimed that they had used materials to get rid of the insects and rodents—one had been forced to remove his home to making pace when swarms had covered their windscreens.

• *Flood story and appeal* [illegible] *page 2; "Sheep Area Inundated," page 7.*

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25.2

Appendix 25a. Cover page of The Advertiser, Adelaide, South Australia, dated Friday, September 28, 1956 describing one of the atomic explosions associated with Operation BUFFALO.

T 57/58

UNCLASSIFIED

Copy No. 403
216 Pages.

UNITED KINGDOM ATOMIC ENERGY AUTHORITY

ATOMIC WEAPONS RESEARCH ESTABLISHMENT

REPORT No. T 57/58

OPERATION BUFFALO

Target Response Tests
(Co-ordinator: E. R. Drake Seager)

Biology Group
(Group Leader: R. Scott Russell)

Part 5: The Entry of Fission Products into Food Chains

Edited by:

J. F. Loutit
(MRC. AERE)

R. Scott Russell
(Radiological Laboratory)

A.W.R.E.,
Aldermaston, Berks.

UNCLASSIFIED

May, 1959

25.3

Appendix 25b. Cover page of Atomic Weapons Research Establishment, Report T57/58, United Kingdom Atomic Energy Establishment - 1959.

PROGRESS IN NUCLEAR ENERGY

SERIES VI

BIOLOGICAL SCIENCES

Volume 3

The Entry of Fission Products into Food Chains

Editors

J. F. LOUTIT

M.R.C. Radiobiological Research Unit, Harwell

R. SCOTT RUSSELL

A.R.C. Radiobiological Laboratory, Letcombe Regis

PERGAMON PRESS
OXFORD · LONDON · NEW YORK · PARIS
1961

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SUMMARY

(a) Investigations carried out both at Maralinga during Operation Buffalo and in the United Kingdom are described.

(b) The extent to which fallout was retained on pastures of types familiar in European agriculture was variable but, when the particle size of the deposition was relatively small, 15–20% of the deposit was found on the foliage. Less retention is, however, likely when a deposit is of large particle size.

(c) The retention of fallout by ripe ears of wheat appeared to be a minor source of hazard to man relative to the contamination of pastures grazed by dairy cattle.

(d) The solubility of fallout deposited on the ground surface, and also collected from radioactive cloud by aircraft, was examined. Relatively high solubility, indicative of ready biological availability, was observed in all cases except the near-in ground deposit after a tower shot. Even this material showed appreciable solubility.

(e) Experiments with rabbits and cows showed that the biological availability of fission products collected from the radioactive clouds of three weapons was not significantly reduced by its physical form. Some evidence was obtained that the same was true for the near-in ground deposit after a ground shot (Round 2).

(f) Studies of the metabolism of fallout by sheep, rabbits and cows confirmed expectations that isotopes of iodine and strontium are the major sources of hazard through ingestion. Shorter lived fission products such as tellurium and molybdenum were metabolized to an appreciable extent; they were, however, shown to be minor sources of hazard relative to the isotopes of iodine and strontium.

(g) The extent to which different isotopes of iodine contribute to the dose to the thyroid soon after the detonation of a weapon was examined.

(h) The results indicate that valid conclusions regarding the metabolism by animals of fission products from fallout can be reached by laboratory experiments using soluble preparations of chemically separated isotopes.

EDITORIAL NOTE

The papers presented in this volume were originally issued as reports by the United Kingdom Atomic Energy Authority, Atomic Weapons Research Establishment, Aldermaston.

Chapters 1–8 are taken from A.W.R.E. Report No. T57/58 Operation Buffalo, Part 5. The editors wish to thank the Director, Atomic Weapons Research Establishment, for permission to publish both the earlier work and Chapters 9 and 10.

SECTION 1: INTRODUCTION

THIS report contains the results of investigations of the movement of fission products into food chains which were undertaken in connexion with Operation Buffalo. The work was sponsored jointly by the Medical and Agricultural Research Councils, with the exception of the study of the contamination of cereals, which was proposed by the Ministry of Agriculture, Fisheries and Food.

The retention of fallout on vegetation, its solubility and its metabolism by animals were investigated at Maralinga by members of the Biological Target Response Group (Sections 2, 6 and 7 of this report). In addition, fallout was collected in filters carried by aircraft and sent by air to the United Kingdom for more detailed studies of metabolism by animals; these studies were conducted at the Medical Research Council Radiobiological Research Unit (Section 4) and the Agricultural Research Council Radiobiological Laboratory (Sections 3 and 5). In collaboration with the Ministry of Agriculture, Fisheries and Food, the latter laboratory also examined the extent of contamination of cereals which had been exposed at Maralinga (Section 3). The results of the investigation as a whole are reviewed in Section 8.

Apart from the members of the staff of the two Research Councils and their collaborators in the United Kingdom and Australia whose names appear as authors of Sections of this report, many others contributed to the work. The investigations with cultivated plants and with animals at Maralinga necessitated considerable preparations before the United Kingdom staff reached Australia. The Commonwealth Scientific and Industrial Research Organization co-ordinated these arrangements. Dr. F. R. G. White, then Chief Executive Officer, CSIRO, the late Prof. J. G. Wood, Chairman of the South Australian Committee of CSIRO and Mr. H. R. Marston, FRS, Chief of CSIRO Division of Biochemistry and General Nutrition, acted as general advisers; Mr Angus Packham, Technical Secretary of CSIRO Division of Biochemistry and General Nutrition, undertook administrative duties. Special metabolism cages for studies with sheep were designed by Mr. Marston who also provided the sheep from his laboratory and seconded two members of his staff, Messrs. I. G. Jarrett and B. J. Potter, to supervise their maintenance. Over 250 boxes containing growing pasture plants of European types were prepared in Adelaide under the direction of Prof. C. D. Donald. Messrs. N. Ford (CSIRO) and G. Sharman (University of Adelaide) collected biological specimens from a base at Emu during the operation.

Considerable voluntary assistance was given at Maralinga by officers of the Indoctrinee Force.

The writers of this report record their thanks for all the assistance they received.

SECTION 7: RADIOACTIVE ISOTOPES IN ANIMAL THYROIDS

By P. DUNN
Department of Supply, Australia

SUMMARY

(a) By means of a recording single channel γ-spectrometer the following isotopes have been identified in the thyroid of sheep fed on fission products from a nuclear explosion: ^{131}I, ^{133}I, ^{133}Xe and ^{135}Xe. In one case ^{132}Te has been identified; this confirms the presence of ^{132}I.

(b) During the period up to $F + 96$ hr short-lived isotopes of xenon and iodine contribute largely to the total activity in the thyroid. After $F + 96$ hr the activity ratio of ^{131}I was similar to that calculated by Dale[6].

(c) It has been shown that the radiation dose to the thyroid due to the isotopes of xenon would be insignificant compared to the dose due to ^{131}I and ^{133}I.

(d) The activities of the isotopes of iodine and xenon in the thyroid at the time of sacrifice have been assessed from the γ-spectrograms and the activity ratio $^{131}I + ^{133}I$ to ^{131}I compared with the theoretically predicted figure of Dale[6].

(e) Comparisons have been made of the relative efficiency of detection of ^{131}I activity in the thyroid using scintillation and M6 liquid counters. The well-type γ-scintillator set on a narrow channel to measure the maximum of the main γ-energy peak was considerably more efficient.

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7.1. INTRODUCTION

IN THE course of a study on the effect of fission products from nuclear explosions upon animals and plants, thyroid samples containing radioactive isotopes became available for investigation. This section discusses the methods used for identifying the various radioactive isotopes in the thyroid and attempts made to estimate their relative abundance.

Radioactivity in thyroids has been measured either by use of the M6 "liquid" type Geiger counter, or else by a well-type γ-scintillator. By plotting radioactivity decay curves certain radioactive nuclides may be identified. The former

method does not, however, permit the energy of the radiation to be determined and relative abundance derived from decay measurements are liable to appreciable error.

The energies of the principal γ-rays emitted were therefore determined and the nuclides responsible for these identified from the decay schemes given by Hollander *et al.*[1] Repeated measurements of the γ-ray distribution enabled the decay rates of the composite activities to be obtained; confirmatory evidence on the fission products present in the thyroids was thus obtained. Moreover, the relative abundance of each nuclide was also deduced from the maximum counting rates, the crystal response factor and the decay scheme for the respective nuclides.

7.2. EXPERIMENTAL METHODS

Fission products derived from a nuclear weapon exploded on the ground, were obtained either as natural fallout on herbage or else in filters on aircraft flying through the radioactive cloud. The fission products were fed to sheep in metabolism cages according to the plan shown in Table 53.

TABLE 53

Animals Used in Thyroid Experiment

Animal no. (sheep)	Time of feeding, $F+$ (hr)	Material fed	Method of feeding	Time of sacrifice, $F+$ (hr)	Thyroid weight (g)	Dilution
1	8	Cut herbage	Natural	16·5	3·0	5/100
2	8	Cut herbage	Natural	42	5·2	5/100
3	8	Cut herbage	Natural	90	2·9	5/100
7	73	High-cloud filter paper extract	By tube to rumen	96	2·7	5/100
4	8	Cut herbage	Natural	137	3·8	5/50
8	73	High-cloud filter paper extract	By tube to rumen	160	4·4	5/50
9	73	High-cloud filter paper extract	By fistula to abomasum	162	6·5	5/50
10	73	High-cloud filter paper extract	By tube to rumen	186	2·7	5/50
5	25	Cut herbage	Natural	259	3·3	Whole thyroid
6	25	Low-cloud filter paper	Mixed with feed	262	3·5	Whole thyroid

Average weight of thyroid for ten animals: 3·8 g.
F = time of fission.

The animals were fed at various times after fission and sacrificed after varying intervals. The majority of the thyroids were dissolved in 2N NaOH and a 5·0 ml aliquot was taken for assay. The aliquots were placed in small

polythene containers and sealed with screw caps. With sheep no. 5 and no. 6 whole thyroids were placed in the containers.

Certain other thyroids were also available. Some had been obtained from sheep on stations at considerable distances from Maralinga: some were derived from animals kept at Maralinga and fed with fission products but which for one reason or another were insufficiently radioactive to be of experimental value apart from their thyroids. These glands were examined and used for comparison of two methods of assay (see Table 57).

The sodium iodide γ-scintillation crystal (type 10f-10515: Harshaw, U.S.A.) was 2 in. in diameter and $1\frac{3}{4}$ in. high with a well 1 in. in diameter in which the polythene containers were placed. Variations in the response of the counter due to temperature changes made daily calibration against ^{131}I standards necessary. The variable bias potentiometer in the single-channel pulse amplitude analyser (Dynatron Radio Ltd., Type N/101) was coupled to the driving mechanism of the recorder chart. When a pulse-height analyser (0·5 V channel width) was employed the background counting rate was 0·083 count/sec while the counting rate for ^{131}I was 1352 counts/sec per μc.

The customary settings of the principal controls of the spectrometer were as follows: The pulse amplifier (Isotope Developments Ltd. Wide Band Analyser Type 652) was capable of delivering a linear output of 40 V into the pulse amplitude analyser and was operated on a differentiating time constant of 3·0 μsec. In the analyser the discriminator bias "sweep" was 45 V and the channel width 0·5 V. Each bias sweep occupied the greater part of the width of a chart on the Honeywell–Brown recorder. A recording period of 0·5 hr corresponded to an integration time in the ratemeter (Ekco Electronics, Type N522A) of 5 sec. To facilitate the comparison of successive spectra the standard settings of the spectrometer were altered as little as possible between recordings.

The γ-radiation energy (MeV) and the discriminator bias (chart reading) were determined by identifying the main energy peak of the following standard sources: ^{131}I (0·364, 0·637 MeV), ^{95}Zr (0·717 MeV) and ^{140}Ba (0·16, 0·30, 0·54 MeV). The range of energies which could be detected by the equipment at the settings used in the present survey was 0·07–0·9 MeV.

The efficiency of detection by the crystal was determined using standard samples of ^{131}I and ^{95}Zr. In each case a polythene container containing a 5·0 ml aliquot was used. The curve obtained (peak height in counts/sec per μc v. γ-energy) was extrapolated back to an energy of 0·08 MeV in order to make an estimation of the photoelectric detection efficiency of ^{133}Xe. The results are given in Table 54 and they agree with those given by Peirson[2].

7.3. RESULTS

^{131}I (0·364 MeV), ^{133}I (0·54 MeV), ^{133}Xe (0·081 MeV) and ^{135}Xe (0·25 MeV) were identified in thyroids by energy determinations and confirmed by decay

rates. The relatively short half-life of ^{135}Xe (9·2 hr) and its parent ^{135}I (6·7 hr) enabled this xenon isotope to be assessed only in one thyroid—sheep no. 1 sacrificed at 16·5 hr after the detonation of the weapon. Because of its γ-energy (1·27 MeV), ^{135}I could not be recorded on the charts using the normal operation

TABLE 54

Calibration and Conversion Factors for Iodine and Xenon Isotopes

Isotope	Main γ-energy (MeV)	$T\frac{1}{2}$	Abundance (%)	Counter efficiency at main energy peak (counts/sec per μc)	Factor for assessment, f
^{131}I	0·364	8·05 days	80	1690	$7{\cdot}4 \times 10^{-4}$
^{133}I	0·54	20·8 hr	94	1330	$8{\cdot}0 \times 10^{-4}$
^{133}Xe	0·081	5·27 days	97·6 {36% / 64% i.c.	2000	$14{\cdot}3 \times 10^{-4}$
^{135}Xe	0·25	9·2 hr	96	1780	$5{\cdot}9 \times 10^{-4}$

conditions for the spectrometer. The short half-life of ^{134}I (53 min) precluded its identification. In one case a peak corresponding to ^{132}Te (0·23 MeV) was found in the spectrogram obtained from the thyroid of sheep no. 2, 44 hr after fission. This isotope was not identified on any other occasion.

The spectrograms for the thyroid of animal no. 1 taken at 29·5 hr and 124 hr after fission are reproduced in Figs. 37 and 38. In the interval between the recording of the two spectrograms the contribution of ^{135}Xe dropped by radioactive decay, and ^{133}I decreased relative to ^{131}I. The settings on the spectrometer during the recording of the spectrograms are given in Table 55.

TABLE 55

Spectrogram Chart Data

Thyroid from sheep no. 1	Fig. 37	Fig. 38
Completion time of chart (hr)	$F + 29{\cdot}5$	$F + 124$
Counting rate, counts/sec channel width	100	10
Channel width (V)	0·5	0·5
Time constant (sec)	5	20
Scanning rate (min)	30	30
E.H.T. (V)	900	900

In all cases spectrograms were recorded at regular intervals until the short-lived isotopes had disappeared into the base-line or became merged into neighbouring peaks.

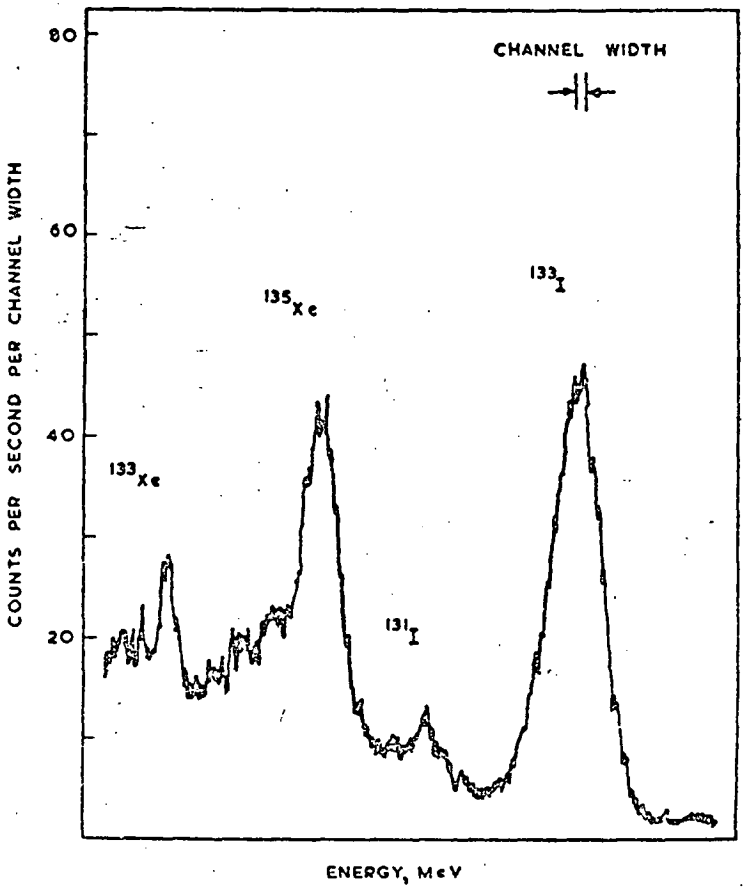

FIG. 37. Spectrometer record of animal no. 1 at 29·5 hr after fission.

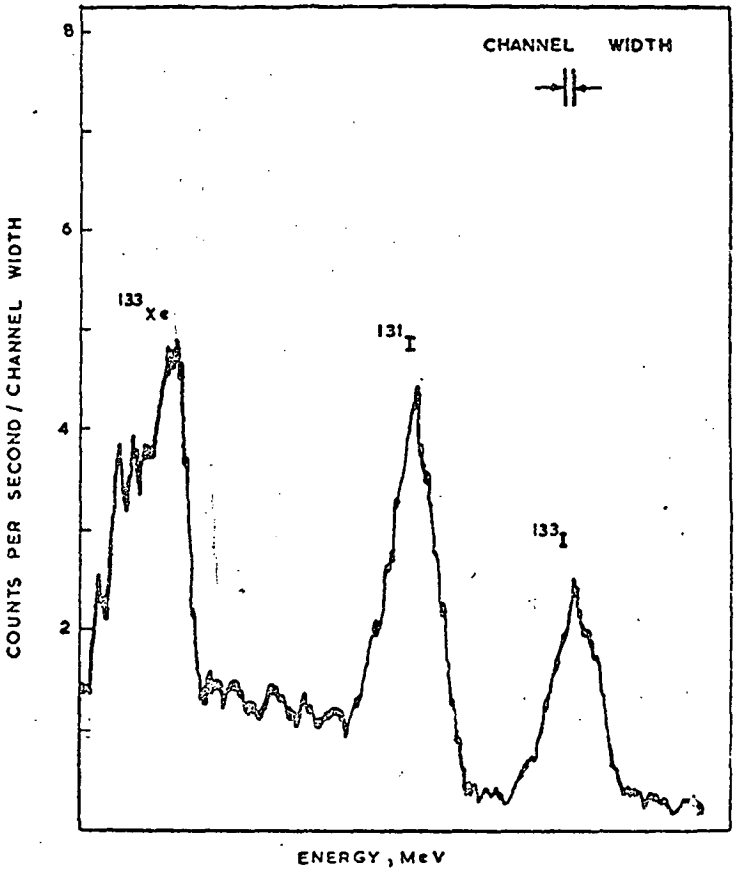

FIG. 38. Spectrometer record of animal no. 1 at 124 hr after fission.

The assessment of the spectrograms recorded from each thyroid enabled the variation of the height of peaks (after adjustment for Compton scatter) at the difference energies to be plotted against times after fission. The radioactive half-life of the nuclide as determined from the slope of the appropriate decay plot confirmed its presence. Typical decay plots for ^{131}I, ^{133}I and ^{135}Xe from the thyroid of animal no. 1 are shown in Fig. 39. Peak heights extrapolated back

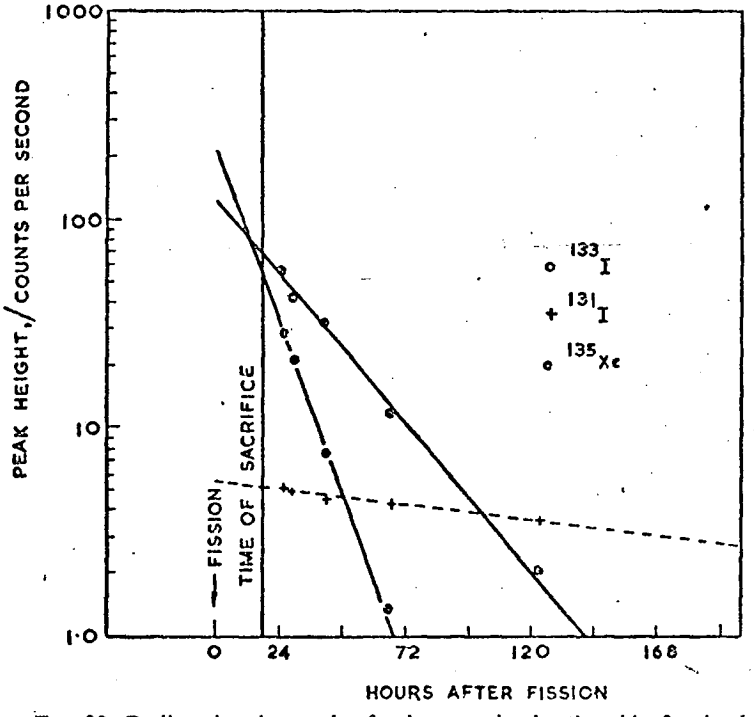

FIG. 39. Radioactive decay plot for isotopes in the thyroid of animal no. 1.

to the time of sacrifice were converted into γ-scintillation activities by using the crystal energy calibration factors given in Table 54. The activity of each isotope was determined by the following equation:

$$A = D \times P.H. \times f,$$

where A = activity in μc/thyroid;
D = dilution factor;
$P.H.$ = peak height at time of sacrifice (counts/sec and per channel width);
f = factor for assessment of activity.

The total activity (μc) in whole thyroid of sheep at the time of sacrifice due to ^{131}I, ^{133}I, ^{133}Xe and ^{135}Xe is given in Table 56. This table also shows the percentage abundance of each of these isotopes in relation to the total activity in the thyroid.

7.4. DISCUSSION

7.4.1. *Relative Contribution of Different Isotopes to the Dose to the Thyroid*

Russell *et al.*[3] have made an assessment of the hazard resulting from the ingestion of fallout by grazing animals. They conclude that the contribution from ^{132}I and ^{135}I to the total dose to the thyroid can be neglected over the periods considered. Similarly it is possible to calculate the dose to the thyroid due to the isotopes of xenon.

The total integrated dose (β-particle dose) due to 1·0 μc/g of xenon isotopes in the thyroid can be given by the equation of Russell *et al.*:

$$D = 3{\cdot}1\bar{E}TC$$

where D = total dose to thyroid (rad);
$\bar{E}$ = effective energy of the radiation (MeV);
T = the effective half-life (hr);
C = concentration of activity (μc/g).

With a highly-vascular tissue such as thyroid, it is considered that the biological half-life of the xenon isotopes in the thyroid would not be in excess of 5 min.[4]

TABLE 56

Iodine and Xenon Isotopes in Sheep Thyroid Due to Fission Products from a Ground Burst

(Calculated from the time of sacrifice of each animal.)

Animal no.	Total activity in whole thyroid (μc) ^{131}I, ^{133}I, ^{133}Xe, ^{135}Xe	Isotopic abundance %				Activity ratio $\frac{^{131}I + ^{133}I}{^{131}I}$	Calculated activity ratio $\frac{^{131}I + ^{133}I}{^{131}I}$	Measurements obtained from M6 counters*	
		^{131}I	^{133}I	^{133}Xe	^{135}Xe			Activity ratio $\frac{^{131}I + ^{133}I}{^{131}I}$	Total activity in whole thyroid (μc)
1	1·865	4·1	61·3	?	34·5	16·0	7·00	∞	1·85
2	1·275	12·0	66·4	21·6	0	6·53	4·20	6·50	1·22
3	0·669	30·5	40·4	29·1	0	2·32	1·80	1·97	0·75
7	5·80	42·5	35·4	22·1	0	1·83	1·60	2·08	3·64
4	1·37	87·0	13·0	?	0	1·15	1·17	1·33	0·92
8	6·67	83·3	6·2	10·5	0	1·08	1·10	1·20	5·30
9	5·40	91·5	8·5	0	0	1·09	1·10	1·18	4·35
10	2·97	97·1	2·9	0	0	1·03	1·05	1·10	2·56
5	0·85	100	0	0	0	1·00	1·00	1·00	1·10
6	1·01	100	0	0	0	1·00	1·00	1·00	1·10

* These results were obtained from D. W. H. Barnes (see Barnes and Butterfield, Section 6).

From the ICRP[5] we have:

For ^{133}Xe $\bar{E} = 0{\cdot}18$ MeV;

hence $D = 3{\cdot}1 \times 1/12 \times 0{\cdot}18 = 0{\cdot}046$ rads/μc g

For ^{135}Xe $\bar{E} = 0{\cdot}56$ MeV;

hence $D = 0{\cdot}146$ rads/μc g.

Since the integrated dose due to ^{133}I has been calculated as 36·1 rads/μc g it follows that the contribution to the total dose in the thyroid due to ^{133}Xe is only 0·13% and ^{135}Xe is 0·4% of that due to ^{133}I for a similar concentration of activity. In assessing the total dose to the thyroid due to the isotopes of iodine and xenon it is clear that the dose due to ^{135}I, ^{133}Xe and ^{135}Xe is insignificant compared to that due to ^{131}I and ^{133}I and can therefore be ignored.

In calculating the contribution of different iodine isotopes to the total activity in the thyroid, Russell *et al.* used the data of Dale[6] for the relative amounts of ^{131}I and ^{133}I resulting from the fission of ^{235}U, viz.:

Time after fission	Relative activities		Calculated activity ratio $\frac{^{131}I + {}^{133}I}{^{131}I}$
	^{131}I	^{133}I	
1 hr	21	140	7·70
12 hr	26	180	7·95
1 day	26	130	6·01
4 days	21	13	1·62
7 days	17	1·4	1·08
14 days	9·3	—	1·00

From these results the calculated activity ratios $^{131}I + {}^{133}I$ to ^{131}I for other times after fission were obtained graphically and are shown in Table 56 for comparison with the experimental values. Agreement is close for times greater than $F + 96$ hr. However, during the first 96 hr after fission, the contribution to the total activity in the thyroid of the short-lived ^{133}I was much greater than the predicted figure. Prior to $F + 90$ hr, ^{133}I represented the major nuclide present in the thyroid. A comparison can be made between the results obtained using the γ-spectrometer and those obtained from the use of a Geiger counter (M6) (see Table 56). The two different methods are in reasonable agreement.

Dunning[7] estimated that after $F + 180$ hr the activity due to ^{133}I would be negligible, but that ^{132}I and its precursor would still exhibit some activity. He has also shown that after $F + 45$ hr ^{135}I would have disappeared from the thyroid through normal radioactive decay. The present findings accord with Dunning's conclusions with the exception that ^{132}I appeared to be important only very soon after fission. However, in the present investigation it is likely

TABLE 57

Comparison of Counters for the Measurement of ^{131}I in the Thyroid of Sheep and Goats

Counter		M6 liquid counter (10 ml) M.A. 653			γ-Scintillator 1 in. well (7·5 V channel measuring whole ^{131}I peak)				γ-Scintillator 1 in. well (0·5 V channel measuring maximum of ^{131}I peak)			
Sample no.	Dilution	Corrected counts per min for aliquots diluted 1/5	Background (60 sec)	E.D.†	Corrected counts per 100 sec	Background (100 sec)	E.D.†	R.E.D.‡ (M6 = 1·0)	Corrected counts per 100 sec	Background (100 sec)	E.D.†	R.E.D.‡ (M6 = 1·0)
806	10/50	1079	15	73	238,570	267	895	12·2	34,932	8	4367	60
807	10/50	353	18	21	85,285	254	337	16	12,741	8	1593	76
808	10/50	4750	20	240	1,022,811	250	4100	17	137,710	9	16,411	69
809	10/25	2042	20	102	541,265	250	2170	21	75,880	9	8431	82
810	10/25	1105	19	59	297,906	250	1200	20·4	43,260	9	4807	82
818	10/50	3630	21	174	876,044	232	3780	21·6	114,690	9	12,743	73
823	10/60	4206	17	247	1,053,985	210	5000	20·2	137,770	8	17,221	70
779*	10/25	4·5	20	1·23	1228	214	6·8	27·5	148	10	14·8	60
780*	10/25	0·3	20	1·00	349	206	2·7	13·5	51	9	6·6	33
832	10/15	1·2	18	1·02	327	218	2·5	2·45	48	7	8·0	7·9
833	10/20	28·4	24	2·20	9020	257	3·6	16·5	856	7	123	56
834	10/25	66·5	24	2·95	17,113	223	78	27·5	1598	7	228	77
Average		—	19·7	—	—	236	—	17·8	—	8·3	—	62

* Samples used for measurement on the γ-scintillator were whole thyroids except for animals 779 and 780 of which aliquots equivalent to one-fifth of the thyroid were assayed. The observed values for these animals have been multiplied by 5.

† E.D. the efficiency of detection of the counters is defined as the ratio $\frac{(\text{count} + \text{background})}{\text{background}}$.

‡ R.E.D. is the relative efficiency of detection.

that the close proximity of the main energy peaks for ^{132}I (0·64 MeV) and ^{131}I (0·69 MeV) made it possible to identify ^{132}I only when its abundance was high relative to ^{131}I.

7.4.2. *Comparison of Scintillation and M6 Geiger Counting Procedures for the Measurement of Activity in the Thyroid*

Table 57 shows the results obtained when different counters were used for the measurement of iodine isotopes in the thyroid of sheep and goats. The greater efficiency of the γ-scintillator compared to the liquid-type Geiger counter is apparent. Using the γ-scintillator the whole of the animal thyroid can be taken for assessment while, for the liquid counter the thyroid must be taken into solution and a suitable aliquot (usually 10/50 ml) taken for measurement.

With γ-scintillator either the whole of the ^{131}I peak (0·364 MeV) or only the maximum of the peak may be measured. By use of a narrow band channel the background was reduced to a minimum and consequently efficiency was increased. With the operating conditions for the different counters here employed, the relative efficiency of detection for the γ-scintillator when measuring the whole of the ^{131}I peak was 17·8 and measuring the maximum of the ^{131}I peak was 62 as compared with a value of 1·0 for the M6 Geiger counter. These results indicated that an efficient means of detection of ^{131}I in the thyroid was the use of a γ-scintillator set with a narrow band channel to the maximum of the main γ-radiation energy on the whole thyroid.

REFERENCES

1. Hollander, J. M., Perlman, I. and Seaborg, C. T., *Rev. Mod. Phys.* 25, 469 (1953).
2. Peirson, D. H., The gamma-ray spectrum of fission products from slow neutron irradiation of ^{235}U, *Brit. J. Appl. Phys.* 6, 444 (1955).
3. Russell, R., Martin, R. P. and Wortley, G., *An Assessment of Hazards Resulting from the Ingestion of Fallout by Grazing Animals*, AERE ARC/RBC/5.
4. Loutit, J. F., MRC, Harwell. Personal communication.
5. ICRP, *International Commission on Radiological Protection. Recommendations* (1955).
6. Dale, G. C., *Safety Levels for Contamination from Fallout from Atomic Trials*, AWRE Report No. 0–41/55.
7. Dunning, G. M., Thyroid dose from radio-iodine in fallout, *Nucleonics* 14, No. 2, 38 (1956).

APPENDIX 26 ANALYSIS OF ORGANIC MATERIALS

26a	The Determination of Pentachlorophenyl Laurate Using Electron Capture Gas Chromatography P. DUNN and A.G. KELSO *J. Gas Chromatog.*, 6, 113 (1968)	26.2 - 26.3
26b	The Analysis of Fuel System Icing Inhibitors (FSII) Based on Ethylene Glygol Monomethyl Ether P. DUNN and A.G. KELSO Report 309. Defence Standards Laboratories, Department of Supply, Melbourne, Australia.	26.4 - 26.5
26c	Thermal Analysis of Compounded Poly(Vinyl Chloride) P. DUNN and B.C. ENNIS *J. Appl. Polym. Sci.*, 14, 355 (1970)	26.6 - 26.15
26d	Thermal Analysis of Polyacrylonitrile Part I. The Melting of Polyacrylonitrile P. DUNN and B.C. ENNIS *J. Appl. Polym. Sci.*, 14, 1795 (1970)	26.16 - 26.20
26e	Thermal Analysis of Polyacrylonitrile: Identification of Acrylic Fibres by Differential Thermal Analysis. P. DUNN and B.C. ENNIS *Thermochimica Acta*, 3, 81 (1971)	26.21 - 26.27
26f	Identification of Transparent Materials for Safety Applications. P. DUNN and G.F. SANSOM *Aust. J. Optom.*, 52, 50 (1969).	26.28 - 26.32

he Determination of Pentachlorophenyl Laurate Using Electron Capture Gas Chromatography

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fense Standards Laboratories, Maribyrnong, Victoria, Australia

Abstract

A quantitative method for the determination of penta-orophenyl laurate in wood preservative solutions using ctron capture gas chromatography is described. The thod has advantages over the standard colorimetric thod because of its rapidity, sensitivity, and ability to tinguish between the ester and sodium pentachlorophen- if this is present. Dieldrin which may also be present in od preservative solutions can also be estimated from the romatogram.

Introduction

The combination of gas chromatography and the ctron capture detector for the determination of small concentrations of chlorinated pesticides in a wide range of materials has been described by many authors (1,2, 3, 4) and reviewed recently by Beynon and Elgar (5).

This laboratory was recently concerned with the estimation of the dieldrin content of solutions to be used for the preservation of wood. These consisted generally of a mineral spirits or similar solvent containing

1. Goodwin, E. S., Goulden, R., and Reynolds, J. G., Analyst **86**, 697 (1961).
2. Goodwin, E. S., Goulden, R., Richardson, A., and Reynolds, J. G., Chem. Ind. (London) **1960**, 1220.
3. Lovelock, J. E., Anal. Chem. **35**, 474 (1963).
4. Burke, J. and Guiffrida, L., J. Assoc. Offic. Agric. Chem. **47**, 326 (1964).
5. Beynon, K. I. and Elgar, K. E., Analyst **91**, 143 (1966).

approximately 5 per cent pentachlorophenyl laurate (PCPL) and 0.5 per cent dieldrin.

For the determination of the dieldrin by gas chromatography, dilution of the sample solution was necessary in order to avoid overloading the detector. Hexane (or isooctane) was used at a dilution ratio of 1:1000. In the course of establishing satisfactory operating conditions, it was found that after the dieldrin peak on the chromatogram, a series of peaks, one major and three minor, was obtained which appeared to be characteristic of the PCPL. It was of interest to compare gas chromatographic analysis with the colorimetric method normally used for the determination of PCPL (6).

Experimental

An F & M Model 810 gas chromatograph (containing a 4-ft by ¼-in. o.d. glass column packed with 1.6 per cent silicone gum rubber [SE-30] on Diatoport S) was used with the F & M electron capture detector and with argon containing 5 per cent methane as carrier and purge gas.

Operating conditions were injection temperature 220°C, oven temperature 200°C, and detector temperature 210°C. The flow rate of the carrier gas was 80 ml per minute and the purge gas, 40 ml per minute. The detector voltage was 30 volts at a pulse interval of 15 microseconds.

Results and Discussion

Samples of wood preservative solution diluted with isooctane and examined under the above conditions gave five peaks on the chromatogram. Of these, the first peak with a retention time of 5.9 minutes was due to dieldrin. The retention times of the four later peaks were 7.2, 8.0, 14.8, and 30.4 minutes, the major peak being at retention time 14.8 minutes.

A typical chromatogram is shown in Figure 1. In this chromatogram, DDT (recrystallized, 98 per cent, p, p'-isomer content; 1.0 per cent w/v in the original solution) was used as the internal standard, and its retention time was 9.7 minutes.

Under the same conditions gas chromatograms obtained from hexane solutions of various concentrations of a commercial grade of PCPL all showed this series of four peaks. Vacuum distillation of the PCPL followed by gas chromatography of the resulting distillate and residue showed that the major peak was due to PCPL and that the three minor peaks were due to impurities. These peaks were not due to phenol, 2,4,5-trichlorophenol, pentachlorophenol, or lauric acid, which could be suspected contaminants.

For the quantitative analysis of PCPL, a reference graph of peak area versus concentration for a calibration series of solutions of PCPL in hexane was used. The sample dilution necessary for the determination of dieldrin was also satisfactory for the determination of PCPL. With the operating conditions described, no interference was observed from the solvent used in the original solutions. Solutions of PCPL in hexane at concentrations as low as 1 part per million can be estimated by this chromatographic method.

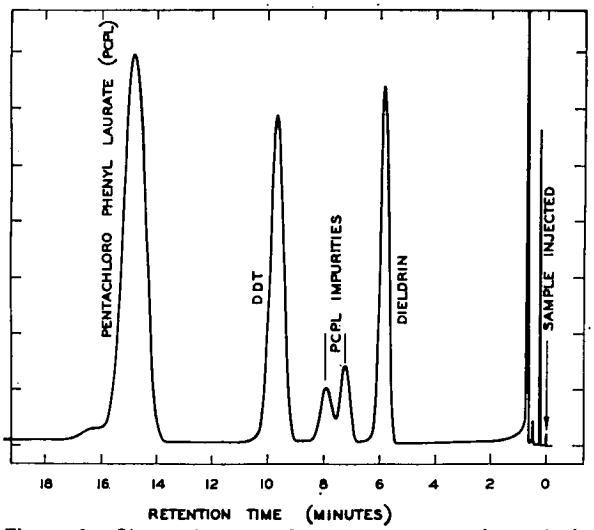

Figure 1. Chromatogram of a wood preservative solution luted 1:1000 in isooctane). Composition (w/v, %): diel (99% HEOD), 0.5; commercial PCPL, 5.0; DDT (internal st ard), 1.0; in white spirit solvent. Injected volume: 3 m liter.

The determination of PCPL by gas chromatogra has several advantages over the standard colorime method as the PCPL content is calculated from same chromatogram as is required for the determina of dieldrin. Often it is desirable to be able to diffe tiate between PCPL and sodium pentachloropl ate, which may be used to replace part or all of PCPL content of a preservative solution. In the sta ard colorimetric method (6), the sample is first drolysed to liberate pentachlorophenol and lauric a as their sodium salts. After acidification, the total p tachlorophenol is determined colorimetrically and differentiation between the ester and the salt is p sible. The solvent used in the preservative solution r indicate the presence of the sodium salt because of different solubility characteristics compared with lauryl ester. The use of the gas chromatograp method, however, leaves no doubt, even though original solvent may not be detected, as no peak is corded for the sodium salt.

By performing the hydrolysis as described in colorimetric method, sodium pentachlorophen PCPL, or the total of a mixture of the sodium salt the lauryl ester may conveniently be determined us gas chromatography. The extracted pentachlorophe can be estimated using a thermal conductivity dete under conditions similar to those reported by Pil (7) for a range of substituted phenols.

Acknowledgment

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6. "British Standards Handbook" Methods of Test of T tiles, No. 11 (1963).
7. Pillion, E., J. Gas Chromatog. 3, 238 (1965).

DEPARTMENT OF SUPPLY
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DEFENCE STANDARDS LABORATORIES

REPORT 309

THE ANALYSIS OF FUEL SYSTEM ICING INHIBITORS (FSII) BASED ON ETHYLENE GLYCOL MONOMETHYL ETHER

P. DUNN and A. G. KELSO

SUMMARY

Quantitative gas chromatographic methods are described for the determination of water in ethylene glycol monomethyl ether (EGME) and of EGME in aviation turbine fuels and in water. The determination of ethylene glycol, glycerol and EGME in aqueous phases associated with such fuels is also described. The methods offer advantages in accuracy, specificity, rapidity and sample size.

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Table 1 - Chromatographic conditions for the analysis of EGME 2

Figure 1 - Calibration curve for the determination of water in EGME

Figure 2 - Calibration curve for the determination of EGME in aviation turbine kerosine (Avtur), using the water extraction technique

Figure 3 - Calibration curve for the determination of EGME in water phases

Figure 4 - Chromatogram of a water phase from a ground fuelling system

APPENDIX 26c
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Thermal Analysis of Compounded Poly(Vinyl Chloride)*

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Synopsis

Differential thermal analysis of mixtures of poly(vinyl chloride) and dioctyl phthalate shows a compound endothermic peak due to decomposition of both polymer and plasticizer. The thermal behavior of other plasticizers is similarly affected in the presence of poly(vinyl chloride). The addition of zinc oxide or ferric oxide decreases the thermal stability of the mixture and, under isothermal conditions, a resultant induction period allows the estimation of an activation energy for the dehydrochlorination of poly(vinyl chloride) and of the relative effectiveness of thermal stabilizer systems.

INTRODUCTION

Poly(vinyl chloride) (PVC) is used extensively in modern construction. While it does not burn readily, it decomposes at relatively low temperatures to give toxic and corrosive products.[1,2] The proportion of the time at recent symposium devoted to this plastic[3] reflects the concern with which this aspect of PVC technology is regarded.

There is limited understanding of the mechanism of degradation of PVC. The dehydrochlorination is generally[4] accepted as being a chain radical reaction, but even under favorable conditions it is not possible to exclude contributing nonradical mechanisms.[5] In the presence of the other components necessary to confer processability and serviceability on the polymer, the degradation will certainly be modified, and perhaps completely changed, in ways that are even less understood.[4,6] Accordingly, the screening and evaluation of compounding ingredients and of PVC formulations are largely empirical exercises and, while the ultimate evaluation must be determined by actual service,[7] various aspects of thermal analysis have recently been suggested for evaluation of thermal stability.

Both thermogravimetric analysis and differential thermal analysis of the polymer have been reported; but, while the expected phenomena of glass transition, dehydrochlorination, and ultimate degradation are obvious, the inherent limitations of thermal methods limit the interpretation of the thermograms. For compounded PVC and for PVC copolymers, the inter-

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action of components modifies the thermograms and meaningful comparisons are possible. Thermogravimetric analysis has been employed by Matlack and Metzger[8] to evaluate the thermal stability of PVC formulations and by Weintraub and his co-workers[9] for comparison of vinyl chloride copolymers. Similarly O'Leary and his co-workers[10,11] have utilized differential thermal analysis. Using these techniques, Dudley and Smith[12] have shown the profound effect of metal oxides on the thermal degradation of chlorinated polymers.

In the present communication we present evidence of the interactions that can occur between PVC, plasticizers, stabilizers, and metal oxides. Under conditions of thermal stress ester-type plasticizers are decomposed in the presence of PVC. Precautions are therefore necessary when interpreting thermoanalytical data for PVC formulations, particularly since there is concurrent decomposition of plasticizer and polymer. In the presence of zinc oxide, an induction period prior to decomposition can be determined under isothermal conditions, and there is evidence that activation energies determined in this way can be used to classify and evaluate stabilizer systems.

MATERIALS AND METHODS

The PVC used was Corvic D65/8 (Imperial Chemical Industries of Australia and New Zealand, Melbourne, Australia), a medium-high molecular weight granular polymer, although other grades of Corvic gave similar results; it was used without further purification.

Commercial plasticizers and stabilizers, Analar zinc oxide, and *B.P.C.*-grade ferric oxide were used as received.

Samples were prepared by ball-milling the solid components; the liquid components were then added by hand mixing and the samples were allowed to equilibrate for a week. McKinney[13] has described the rapid dispersion of plasticizer in PVC when "dry mixed" above 120°C. In the present investigation the dispersion of plasticizer was accomplished during the warm-up period, and any incomplete dispersion of solid components was offset by the known thermal history of the sample.

All differential thermal analyses (DTA) were performed on a DuPont 900 Differential Thermal Analyzer using the standard cell (unweighed samples, 1–2 mg) and a heating rate of 20°C/min. When operating in the isothermal mode, there was a warm-up period of 2–3 min and timing was commenced when the heater voltage fell within 3 volts of the operating isothermal voltage. The isothermal temperature was measured in the glass bead reference material and an atmosphere of oxygen-free nitrogen was used to minimize oxidative effects.

A Stanton Automatic Thermo-recording Balance, Model HT-SM, was used, without modification, for the limited thermogravimetric work. Sample size was 50–100 mg and the heating rate was 6–7°C/min.

RESULTS AND DISCUSSION

The DTA traces of two typical PVC compounds that differed only in that one contained a small amount of ferric oxide as an additive are shown in Figure 1, together with those of the base polymer and dioctyl phthalate (DOP) plasticizer. It can be seen that the endothermic peak due to the boiling of the plasticizer is absent from the thermogram of the compounded

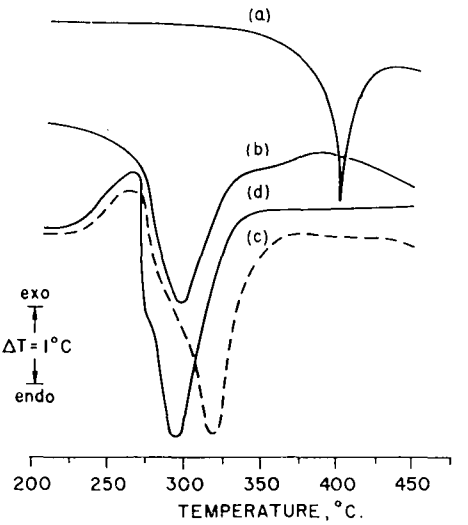

Fig. 1. DTA traces of: (a) dioctyl phthalate on glass beads; (b) PVC (Corvic D65/8); (c) typical PVC compound; (d) same as (c) but containing Fe_2O_3, 1 phr.

material; that the endothermic peak due to the dehydrochlorination of the polymer has been broadened and the peak position shifted; and that, while the deleterious effect of ferric oxide is obvious, both formulated materials shown an early exothermic effect. Similar results are shown in thermogravimetric analysis. These observations have obvious implications in the application of thermal analysis to evaluation studies of PVC additives.

PVC–Plasticizer Interaction

A series of mixtures of PVC and DOP were prepared with increasing amounts of polymer in the plasticizer. The DTA traces (Fig. 2) of typical mixtures are shown. As the amount of PVC was increased, the endothermic peak at 400°C, attributed to boiling of the DOP, was weakened and a new endothermic peak appeared, which strengthened as the peak temperature shifted to lower temperatures. When the DOP concentration was 420 parts per 100 parts resin (phr), there was no indication of the original endothermic peak. A sublimate, identified as phthalic anhydride, appeared on the bell jar at temperatures above 320°C.

The new endothermic peak at temperatures about 350°C can be attributed to decomposition of the DOP. Zilberman and his co-workers[14]

have shown that DOP is decomposed to phthalic anhydride and octenes by prolonged heating with PVC at 170°C, and Stepec et al.[15] found that the energy of activation for the degradation of PVC is dependent on the concentration of DOP present. Under other conditions the susceptibility of DOP (and other plasticizers) to oxidative attack has been noted.[16] In the present case oxidation is precluded, and the stoichiometry (0.73 mole available HCl/ester group) suggests catalytic decomposition of the DOP to phthalic anhydride and octenes, a contention strengthened by results obtained in the presence of metal oxides.

The observed decomposition of plasticizer during DTA in the presence of PVC is not confined to DOP alone, but has also been shown for dioctyl sebacate and tritolyl phosphate. The reported[10] "boiling off" of trioctyl

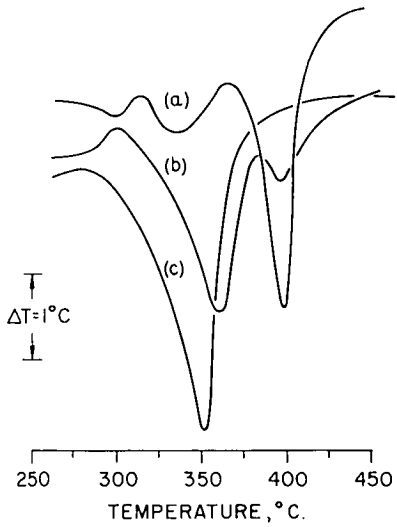

Fig. 2. DTA of PVC–DOP mixtures: (a) DOP, 940 phr; (b) DOP, 520 phr; (c) DOP 420 phr.

phosphate (bp 220°C/5 mm Hg)[17] from a PVC compound at 250°C must also be seen as a decomposition of the plasticizer. Since normal PVC formulations contain considerably less DOP than the mixtures we have been considering, the decomposition of the plasticizer in normal compounds is shifted to lower temperatures. It then coincides with the dehydrochlorination of the polymer and modifies both peak position and shape (Figs. 1 and 2) in the thermogram. Any estimation of the relative thermal stability of plasticized PVC from the peak temperature of the dehydrochlorination reaction, as recommended by O'Leary,[11] must be treated with extreme caution. Both energies of activation (derived from peak shape) and enthalpies of decomposition (derived from peak area) can contain an appreciable contribution from plasticizer decomposition.

Effect of Metal Oxides

While the deleterious effect of ferric oxide on PVC (Fig. 1) is well known, Smith and Dudley[12] found that, in the presence of ferric oxide, the thermograms of chlorine-containing polymers, including PVC, show an additional exothermic peak before the dehydrochlorination reaction. Further, under isothermal conditions, this peak was subject to an induction period and the derived activation energies could be correlated with the activation energy for dehydrochlorination of the polymers. While we were unable to reproduce these effects for simple mixtures of ferric oxide and PVC, corresponding results were obtained when DOP was added to the mixture.

Repetition of the previous DTA with the addition of small amounts of ferric oxide to the mixture of PVC and DOP showed the extent of the effect of the oxide. Reaction occurred at a much lower temperature and the

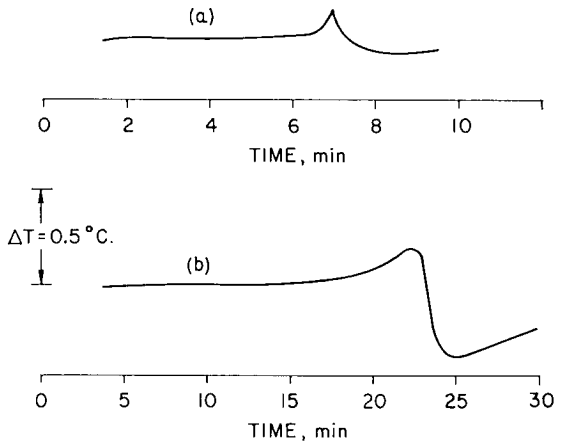

Fig. 3. Isothermal DTA of PVC–DOP (70 phr) mixtures: (a) Fe_2O_3, 2.0 phr, at 204°C (b) ZnO, 3.6 phr, at 164°C.

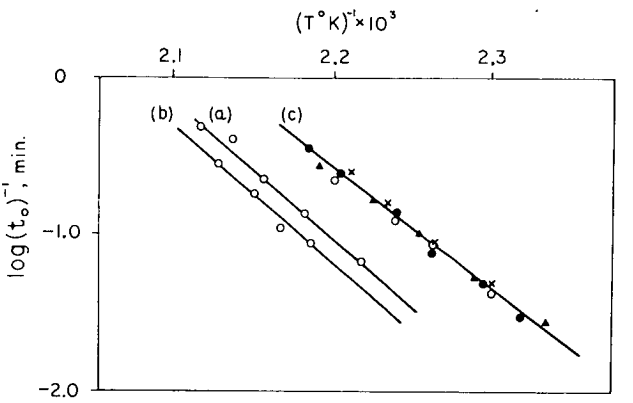

Fig. 4. Arrhenius plot for the induction period of PVC–DOP (70 phr) and metal oxide mixtures: (a) Fe_2O_3, 1.0 phr; (b) Fe_2O_3, 2.0 phr; (c) ZnO: (×), 1.0 phr; (●), 1.8 phr; (▲), 3.6 phr; and (○), 7.8 phr.

boiling of the DOP was completely suppressed by the presence of 0.025 mole ferric oxide and 0.15 mole PVC (monomer equivalent). Similar results were obtained for dioctyl sebacate and tritolyl phosphate plasticizers. Ferric oxide alone, or in conjunction with thermally dehydrochlorinated PVC, was ineffective in promoting decomposition of the plasticizers.

Under isothermal conditions it was found that, after an induction period, mixtures of ferric oxide, PVC, and DOP (70 phr) underwent an exothermic reaction which was immediately followed by an endothermic reaction (Fig. 3). The induction time (t_0) was taken as the time to the initial exothermic departure from the baseline. This gave a straight line for the Arrhenius plot, whereas the time to maximum exotherm or maximum endotherm did not.

Change of DOP concentration in the range 50–100 phr did not affect the induction time; however the Arrhenius plot had the same dependence on ferric oxide concentration (Fig. 4) as was observed by Smith and Dudley[12] in the absence of plasticizer.

When ferric oxide was replaced by zinc oxide, the induction period was reduced and the thermal effects increased in magnitude. The effect of concentration of zinc oxide on the induction period was slight (Fig. 4).

In a very limited thermogravimetric investigation it was found that under isothermal conditions the rate of weight loss from these mixtures was much greater for those containing zinc oxide than for those with ferric oxide, and that in the case of the former it was apparently proportional to the initial concentration of the zinc oxide. However, the induction period could not be determined with the same degree of accuracy as found in differential thermal analysis.

The derived energies of activation from the Arrhenius plots (Fig. 4) are 36 and 33 kcal/mole for reactions in the presence of ferric oxide and zinc oxide, respectively. Both values are of the expected order for the dehydrochlorination of PVC.[12]

The DTA results can be interpreted as being determined by the initial thermal degradation of PVC. The evolved hydrogen chloride, and metal halide when metal oxide was present, is seen as acting as an acid catalyst for the decomposition of the polymer[12] and the plasticizer[14] and perhaps for the interaction of both. Since they are less volatile, both ferric and zinc chlorides will maintain a higher concentration in the system than hydrogen chloride and thus be more effective. The absence of exothermic effects when there is no plasticizer present is considered to be predominantly a transport effect which would be overcome by the use of sufficiently finely dispersed oxide in the polymer. The interpretation requires an unmodified thermal degradation to proceed until there is some critical catalyst concentration, at which time vigorous reaction of both plasticizer and polymer ensues. While there is unreacted oxide (or stabilizer in the more general case), the net effect is an exothermic reaction; however when these are reacted, the true endothermic nature of the dehydrochlorination is manifested (Figs. 1 and 3 and thermogram[10]).

The pronounced exotherm suggests that very little degradation has occurred at the time of the initial exothermic departure from the isothermal baseline (Fig. 3). If the efficiency of formation of zinc chloride is greater than that of ferric chloride, or if the catalytic effectiveness is greater, than the point of departure will correspond to a smaller degree of decomposition of the PVC. Since the chlorine atoms first eliminated are the most labile, this could account for the decreased energy of activation observed in the presence of zinc oxide.

Evaluation of Stabilizers

With constant plasticizer and metal oxide concentrations, a reproducibly small degree of decomposition of the PVC should have occurred at the end of the induction period. This period will be influenced by the presence of stabilizers in the system and would therefore be expected to reflect their effectiveness.

A mixture was chosen such that induction periods could be determined in the range 160°–220°C, and calcium stearate, dibasic lead phosphite, and dibutyltin dilaurate, representing poor, moderate, and good stabilizers, respectively, were incorporated into the formulation, as follows: PVC (Corvic D65/8), 100 parts by weight; dioctyl phthalate, 70 parts by weight;

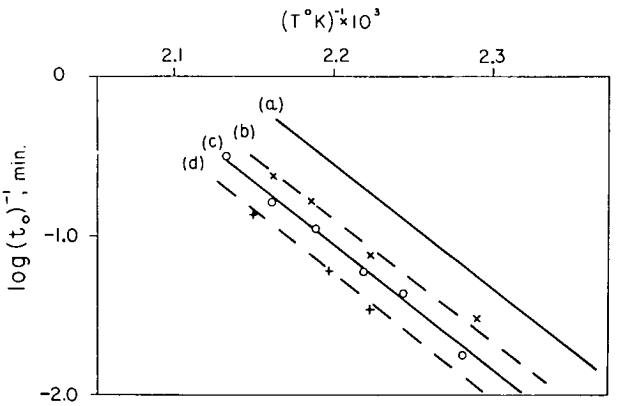

Fig. 5. Arrhenius plot for PVC–DOP (70 phr), ZnO (1.8 phr), and calcium stearate mixtures: stabilizer concentration (a) 0.0 phr; (b) 1.1 phr; (c) 2.1 phr; (d) 3.2 phr.

zinc oxide, 1.8 parts by weight; and stabilizer, equivalent weights, as shown. Arrhenius plots were constructed from the induction times determined for different levels of stabilizer concentration.

Straight-line relationships with both calcium stearate (Fig. 5) and dibasic lead phosphite (Fig. 6) were obtained, and the displacement of the graphs showed a marked concentration dependence. The apparent activation energy was the same as in the unstabilized mixture in each case; however the stearate was marginally less effective in increasing the induction period. This suggests that these stabilizers have little effect on the initiation reac-

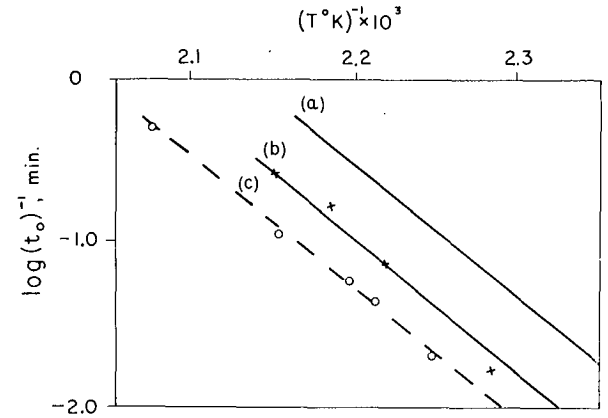

Fig. 6. Arrhenius plot for PVC–DOP (70 phr), ZnO (1.8 phr), and dibasic lead phosphite mixtures: stabilizer concentration (a) 0.0 phr; (b) 1.0 phr; (c) 1.8 phr.

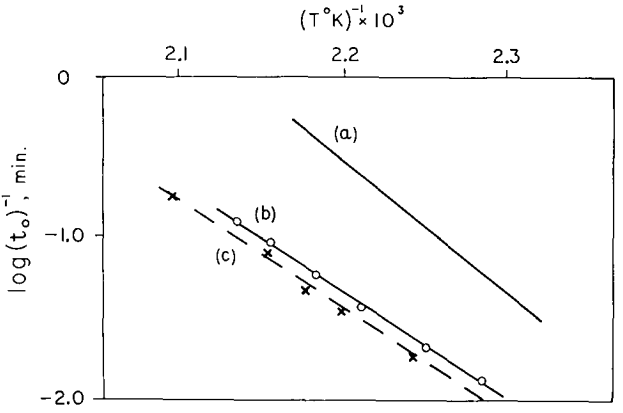

Fig. 7. Arrhenius plot for PVC–DOP (70 phr), ZnO (1.8 phr), and dibutyltin dilaurate mixtures: stabilizer concentration (a) 0.0 phr; (b) 1.1 phr; (c) 2.2 phr.

tions in the degradation, but function as simple hydrogen chloride acceptors.

In contrast, the compound containing dibutyltin dilaurate showed a lower energy of activation (31 kcal/mole) than the unstabilized mixture (33 kcal/mole) (Fig. 7). Also an increased concentration of the organotin stabilizer had much less effect than the former stabilizers. O'Leary et al.[11] reported decreased heat of dehydrohalogenation for PVC in the presence of organotin stabilizers, and Metzger[8] noted that, while the onset of weight loss was delayed by organotin stabilizers, the ultimate reaction was more vigorous. It is therefore apparent that these stabilizers function directly at the initiation of degradation.

The synergism of a mixture of calcium stearate and dibutyltin dilaurate was also shown (Fig. 8) by this method. The observed induction period

was longer than that predicted by simple addition of the increments due to each component. It is interesting to note, however, that the gradient of the line approximated closely to that predicted.

In the absence of the "destabilizing" zinc oxide, DTA of the above mixtures, at linear heating rates, gave traces in which it was difficult to pick with certainty the onset of degradation. The traces showed only small differences in endothermic peak temperature and isothermal studies were not attended by sufficiently pronounced thermal effects to be useful.

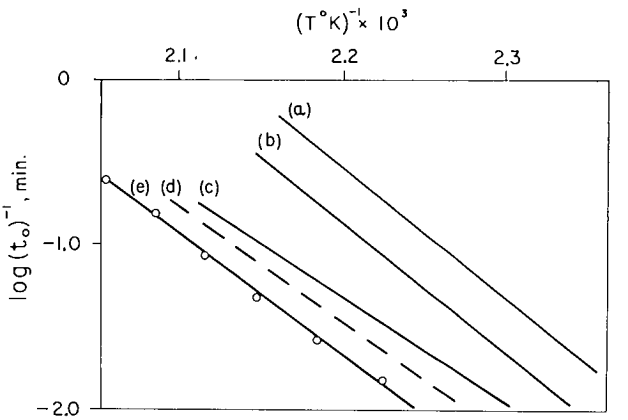

Fig. 8. Arrhenius plot for PVC–DOP (70 phr), ZnO (1.8 phr), dibutyltin dilaurate, and calcium stearate mixtures: (a) no stabilizer; (b) calcium stearate, 1.1 phr; (c) dibutyltin dilaurate, 1.1 phr; (d) calculated (nonsynergistic) value for (b) and (c); (e), measured values for (b) and (c).

On the other hand, the isothermal method using a "destabilizer," such as zinc oxide, gives easily determined endpoints, allows estimation of concentration dependence, and indicates qualitative differences between stabilizer systems. The effect of stabilizers on the decomposition of ester-type plasticizers, leading to flammable by-products during the decomposition of PVC compounds, can also be studied by these techniques.

References

1. E. A. Boettner, G. Ball, and B. Weiss, *J. Appl. Polym. Sci.*, **13**, 377 (1969).
2. Y. Tsuchiya and K. Sumi, *J. Appl. Chem.*, **17**, 364 (1967).
3. SKYDD 69, Plastics—Fire—Corrosion, *International Symposium on Corrosion Risks in Connection with Fire in Plastics*, Sponsored by Research Foundation of the Swedish Fire Insurance Companies, Stockholm, April 24, 1969.
4. W. C. Geddes, *Rubber Chem. Technol.*, **40**, 177 (1967).
5. C. H. Bamford and D. F. Fenton, *Polymer*, **10**, 63 (1969).
6. M. B. Niemann, Ed., *Ageing and Stabilization of Polymers*, Consultants Bureau, New York, 1965.
7. S. Cohen, *SPE 22nd Tech. Conf., Tech. Papers*, Vol. 12, Stanford, Conn., 1966, Session 24, Paper No. 6.
8. J. D. Matlack and A. P. Metzger, *J. Appl. Polym. Sci.*, **12**, 1745 (1968).
9. L. Weintraub, J. Zufall, and C. A. Heiberger, *Polym. Eng. Sci.*, **8**, 64 (1968).

10. R. K. O'Leary, J. Foy, W. L. Guess, and J. Autian, *J. Pharm. Sci.* **56**, 453 (1967).
11. R. K. O'Leary, J. Foy, W. L. Guess, and J. Autian, *J. Pharm. Sci.*, **56**, 494 (1967).
12. M. A. Dudley and D. A. Smith, in *Advances in Polymer Science and Technology*, S.C.I. Monograph No. 26, Society of Chemical Industry, London, 1967, p. 49.
13. P. V. McKinney, *J. Appl. Polym. Sci.*, **11**, 193 (1967).
14. E. N. Zilberman, O. D. Strizhakov, and E. M. Peepletchikova, *Plast. Massy*, 29 (1965); *Chem. Abstr.*, **64**, 8392 (1966).
15. J. Stepec, I. Franta, and B. Dolezel, *Mod. Plast.*, **40**, 147 (1963).
16. I. Wolkober and I. Varga, *Kunststoffe*, **57**, 895 (1967).
17. D. N. Buttery, *Plasticizers*, Cleaver-Hume Press, London, 1957, p. 29.

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APPENDIX 26d
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Thermal Analysis of Polyacrylonitrile. Part I. The Melting of Polyacrylonitrile

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Synopsis

The melting point of polyacrylonitrile can be determined directly by differential thermal analysis, provided that a sufficiently fast heating rate is used. The experimental value of 326°C agrees well with predicted values of the melting point. The disparity between oxidative and thermal decomposition of the polymer is noted.

INTRODUCTION

The thermal decomposition of polyacrylonitrile (PAN) is not a simple reaction. Hay[1] considers that at least three distinct reactions are competing in the purely thermal decomposition, while Friedlander and co-workers[2] have demonstrated the complexity of the oxidative discoloration reaction.

The effect of these reactions in differential thermal analysis (DTA) is an exotherm, at about 300°C, of such magnitude that, in normal practice, only major thermal effects are unequivocally identified. Schwenker and Beck[3] studied the DTA of PAN and Orlon and reported the exotherm, and Thompson[4] has shown that the shape and position of the exotherm is influenced by the molecular weight of the polymer. Recently Slade[5] has shown that a relatively small endotherm, before the main exotherm, can be assigned to the melting point in acrylonitrile–vinyl acetate copolymers. Using the Flory relationship he extrapolated from the melting point of these copolymers a melting point for PAN of 322°C, which was in good agreement with the value of 317°C determined by Krigbaum and Tokita[6] using dilatometric methods.

In the present work it is shown that, at sufficiently fast heating rates, DTA allows direct determination of the melting point of PAN before gross reaction occurs. Some observations are made on the thermal decomposition of PAN and a possible second-order transition is noted.

EXPERIMENTAL

Polyacrylonitrile (PAN). The polymer was obtained from the Mitsubishi Rayon Company Limited as a continuous filament fiber. Finish oils were removed from the fiber by ethanol–benzene (1:2) extraction.

Thermal Analysis. The thermograms were obtained on a du Pont Model 900 differential thermal analyzer system. For the isothermal studies, and the associated dynamic thermograms at a heating rate of 20°/min, the standard cell assembly was used; an unweighed fiber sample was wound closely around the thermocouple and inserted in the 2-mm sample tube. An oxygen-free nitrogen atmosphere and a glass bead reference sample were used, and the timing of the induction period was as previously described.[7] In dynamic studies in air, the DSC cell was used. In this case the unweighed sample was chopped into short lengths and encapsulated in crimped aluminum pans to obtain maximum thermal contact. An empty pan provided the reference.

DISCUSSION

In dynamic DTA studies it was shown that changing the atmosphere from air to nitrogen had only a small effect on the thermograms before the onset of exothermic decomposition of PAN and Orlon.[3,8] There are major differences between the oxidative[2] and thermal[1] decompositions of PAN, and these are more obvious in isothermal DTA studies.

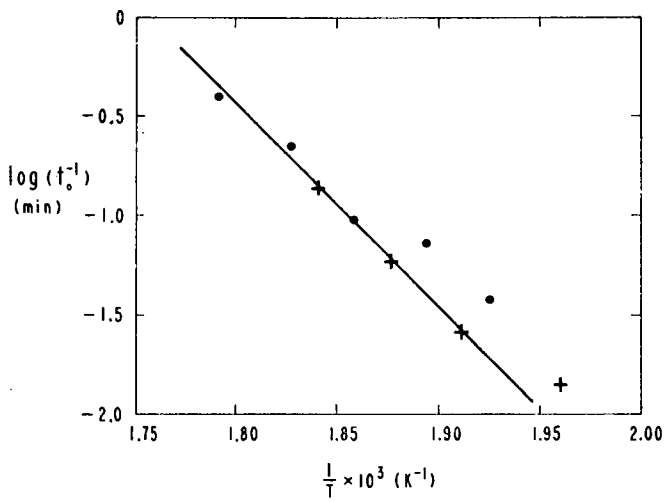

Fig. 1. Arrhenius plot for the induction period (t_0) of PAN, under N_2, at temperature T: (+) present data; (●) data from Hay[1].

As reported by Hay[1] the thermal decomposition of PAN in an inert atmosphere is characterized by an induction period, and an Arrhenius plot of this time against temperature allows an estimation of the activation energy of the reaction. Figure 1 shows this plot, both for our own figures and those of Hay. The given line corresponds to an activation energy of 44 kcal/mole and this, it is suggested, is a more realistic figure than that of 30 kcal/mole as previously quoted.[1] The departure from the straight line at

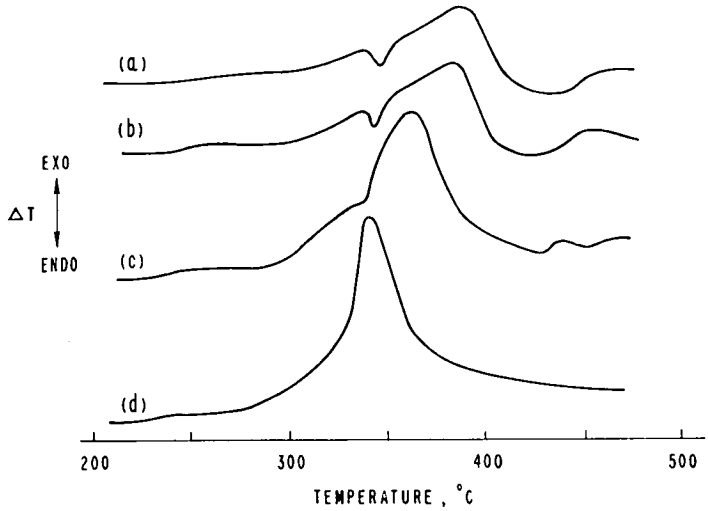

Fig. 2. Effect of heating rate on the DTA of PAN (bracketed figures give relative increase in ΔT sensitivity); (*a*) 100°C/min; (*b*) 80°C/min; (*c*) 40°C/min^{-1} (×2), (*d*) 20°C/min (×4).

lower temperatures could indicate the presence of a different reaction with a lower activation energy.

Samples of PAN that have been heated isothermally, at temperatures between 240° and 280°C, until completion of the exothermic reaction show no exothermic effects on subsequent dynamic DTA. The material behaves completely differently in air. Not only is there no autocatalytic exothermic reaction when PAN is heated isothermally in air at temperatures between 240° and 280°C for equivalent times, but, after cooling, subsequent dynamic DTA still shows the exothermic effect at 300°C. There is some reduction of the intensity of the exotherm which is dependent on the time and temperature; more prolonged isothermal treatment in air results in a progressively broader and flatter exotherm.

It is apparent that the oxidative decomposition of PAN is slower than the purely thermal reaction and, furthermore, that the presence of air actively inhibits the latter reaction, but not its potential occurrence. Since the thermal reaction is considered to be an autocatalytic cyclization reaction,[1] it is obvious that oxidation of either the initiation sites or the initial reactive intermediates prevents the propagation of the exothermic thermal reaction in air. Mechanisms proposed for degradation of PAN in air will have little relevance to those in an inert atmosphere, and vice versa.

From Figure 1, the induction time for thermal reaction at 300°C would be expected to be about 1 min, and oxidative degradation proceeds more slowly or with less disruption of the original polymer structure. Thus, if the rate of heating is sufficiently great, the melting of PAN should be observed before appreciable reaction can supervene. Figure 2 shows the thermograms of PAN in air, obtained from the DSC cell which allows controlled

heating at rates up to 100°C/min. The melting point is best approximated by the temperature of onset of endothermic deflection from the baseline of the thermogram rather than the point of maximum deflection, in contrast to the standard cell. The observed melting point of PAN is thus 328°, 327°, and 326°C, at heating rates of 100°, 80°, and 40°C/min, respectively. The relative insensitivity of the effect to change of heating rate is a clear indication of a first-order transition; the slight variation is inherent in the cell design. The best value is probably 326°C since, although more decomposition occurs before melting at the lower heating rate, the discrepancy between true and indicated sample temperature will be greater at the faster heating rates. This melting point is in good agreement with the predicted values of 317°C[6] and 322°C.[5]

The thermograms (Fig. 2) also show a slight effect at about 240°C, which is insensitive to changes of heating rate between 5° and 100°C/min. This could be attributed to a previously unreported second-order transition for a PAN with a relatively high degree of crystallinity. This should be confirmed. The effect of heating rate on the thermo-oxidative decomposition is also apparent. The melting of PAN is nearly obscured when the rate is 40°C/min; at lower rates decomposition supervenes, while at higher rates the melting is more evident. The change of shape of the thermogram at higher heating rates is indicative of changing reaction mechanisms, and this is consistent with the known heat stabilization of PAN.

At a heating rate of 100°C/min, the melting endotherm of precipitated PAN is appreciably smaller than that of the continuous filament fiber. We expect that for a PAN fiber of given composition, and thus reproducible decomposition characteristics, high heating rate DTA will provide a useful measure of relative crystallinity.

References

1. J. N. Hay, *J. Polym. Sci. A-1*, **6**, 2127 (1968).
2. H. N. Friedlander, L. H. Peebles, J. Brandrup, and J. R. Kirby, *Macromolecules*, **1**, 79 (1968).
3. R. F. Schwenker and L. R. Beck, *Text. Res. J.*, **30**, 624 (1960).
4. E. V. Thompson, *J. Polym. Sci. B*, **4**, 361 (1966).
5. P. E. Slade, Monsanto Company, Pensacola, Florida, Private Communication.
6. W. R. Krigbaum and N. Tokita, *J. Polym. Sci.*, **43**, 467 (1960).
7. P. Dunn and B. C. Ennis, *J. Appl. Polym. Sci.*, **14**, 355 (1970).
8. J. K. Gillham and R. F. Schwenker, *Appl. Polym. Symposia*, **2**, 59 (1966).

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APPENDIX 26e

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THERMAL ANALYSIS OF POLYACRYLONITRILE: IDENTIFICATION OF ACRYLIC FIBRES BY DIFFERENTIAL THERMAL ANALYSIS

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(Received March 26th, 1971)

ABSTRACT

A fast heating rate DTA technique has been applied to various commercial acrylic fibres (Acrilan, Courtelle, Orlon, Cashmillon, Exlan, Creslan, and Acribel). Their melting points, which may otherwise be obscured by exothermic decomposition, can be reliably determined, and the patterns of thermal events obtained by this method can be used to afford some discrimination between commercial acrylic fibres.

INTRODUCTION

Commercial acrylic fibres contain at least 85% acrylonitrile (AN) copolymerised with a small amount of a functional monomer, to provide specific dye sites, and a larger amount of a third, neutral, monomer, such as methyl acrylate, methyl methacrylate or vinyl acetate, to modify the physical properties of the polymer[1]. Fibres containing less than 85% AN are defined as modacrylics[2]. Identification of individual acrylic fibres, and their differentiation from other classes of fibre, requires a combination of both physical and chemical tests[1,3,4]. Coloured fibres present further complications.

Differential thermal analysis (DTA) is an extremely flexible technique for testing small amounts of single or mixed fibres[5,6,7]. The results are not usually influenced by the presence of dyes and pigments. The very strong and sharp exotherm at about 300 °C reported by Schwenker and Beck[8] for Orlon and polyacrylonitrile (PAN) is characteristic for acrylics and may be used to differentiate them from other fibres. The differences between the copolymer and homopolymer were however slight, and no greater than those observed between homopolymers of differing molecular weight[9]. The development of techniques capable of discriminating between homopolymer and various copolymers is thus desirable.

Von Illers[10] studied a series of AN–methyl acrylate copolymers and noted differences in minor thermal effects that were dependent on copolymer content. These small differences would not be detected in routine DTA, and no melting points were found. Slade[11], however, was able to detect the melting point in a series of AN–vinyl acetate copolymers by DTA at 20 °C/min, and we[12] have reported the observation of the melting of PAN by DTA at fast heating rates. The failure to observe the

melting point of acrylonitrile polymers can be attributed to the rapid decompositi of the polymers at relatively slow heating rates, and the much greater magnitude of t heat of reaction in comparison to the heat of fusion. Thus DTA has not been appli to acrylic fibres in the same way as to other crystalline synthetics such as pol ethylene, nylon and poly(ethylene terephthalate). Our previous work[1,2] has sho that fast heating rate technique may afford a means of overcoming these difficulti

EXPERIMENTAL

Materials

The homopolymer PAN and the copolymer COPAN (7% vinyl acetate) we obtained from Mitsubishi Rayon Company Limited. The other fibres (Table II) we obtained from commercial textile suppliers and are identified by Trademark. A samples are normal textile fibres and, although the major comonomer and gene method of preparation may be known, the exact compositions are subject to comm cial secrecy. The samples were of rope or carpet grade fibre, and were used received.

One sample, COPAN, was extracted with boiling ethanol–benzene mixtu (1:2) to remove normal textile finish oils prior to isothermal studies.

Thermal analysis

The DuPont 900 Differential Thermal Analyzer produced by E. I. DuPont Nemours and Co., Wilmington, Delaware was used in these studies. Both the standa DTA cell and the differential scanning calorimeter (DSC) cell were used[13].

Technique

When using the DSC cell, the sample fibre (2–3 mg) was chopped into sh lengths and encapsulated in a lightly crimped aluminium pan so that there w maximum thermal contact between pan and contents. An empty pan was used reference and the atmosphere (air) was not controlled. The nominal heating ra were between 5 and 100°C/min. For the standard DTA cell an unweighed length fibre was wound closely round the sample thermocouple, up to the ceramic sleeve, a inserted into the 2 mm glass sample tube. The DTA curves were obtained at nominal 20°C/min in an atmosphere of air, and glass beads were used as reference. isothermal studies there was a warm up period of 2–3 min and timing was commenc when the heater voltage fell to within 3 V of the operating isothermal voltage. T isothermal temperature was measured in the glass bead reference and an oxygen f nitrogen atmosphere was maintained by a gas flow of 0.75 l/min.

Temperatures given are uncorrected for chromel–alumel thermocouples a the initiation temperatures given for decomposition were determined by detection the initial deviation from the base line. The use of extrapolated onset temperature precluded because the base line is not reestablished after melting (in some cases) a the catalytic nature of the decomposition does not admit a linearized peak: t

nbination of these effects gives an extrapolated onset at least as subjective as any imation of deflection from base line.

SULTS AND DISCUSSION

In DTA it is generally accepted that,while the differential temperature (ΔT) is reased by increasing the heating rate, this improved sensitivity is obtained at the pense of decreased resolution of successive thermal events[14]. However we have own[12] that, in the case of PAN subjected to the fast heating, the DTA curve arly resolves the melting of the polymer (a first order transition which is relatively ensitive to changes of heating rate) from its exothermic decomposition which is fted to higher temperatures. This shift is the complex result of the autocatalytic ure of the decomposition[12,15], the delayed heat transfer at higher heating rates, l the restricted equilibrium resulting from partial retention of volatile products. e DTA curves of the copolymers COPAN and Courtelle (Table I) are similarly

BLE I

CT OF HEATING RATE ON THE MELTING AND DECOMPOSITION OF ACRYLIC FIBRES (DSC CELL)

re	*Heating rate* (°C/min)	*Melting point* (°C, Chromel–alumel)		*Decomposition* (°C, Chromel–alumel)	
		T_0[a]	T_{max}[b]	T_0	T_{max}
N	100	334	346	320	386
	80	333	344	290	383
	40	332	338	280	362
	20			265	340
	5			230	310
PAN	100	250	282	310	392
	80	250	280	[c]	384
	40	245	278	[c]	367
	20	247	278	[c]	335
	5			220	325
rtelle	100	277	288	230	357
	80	275	287	225	349
	40			220	327
	20			195	306
	5			185	275

tiation temperature. [b]Temperature of maximum ΔT amplitude. [c]Decomposition begins during ting.

pendent on the heating rate. The melting point is constant and unaffected by nges of heating rate between 5 and 100°C/min; however decomposition of the ymer can supervene before melting can occur. Thus, at a rate of 100°C/min, the omposition of COPAN does not begin until the melting is complete, but at lower es it begins during melting, and at a rate of 5°C/min it has proceeded to an extent t precludes detection of melting. The melting of Courtelle can only be observed

when the rate of heating is greater than 80°C/min. Since the main copolymer in th fibre is methyl acrylate[16] this explains why Von Illers[10] was unable to detect melting point of AN–methyl acrylate copolymers in DTA studies at 32°C/min.

Typical thermograms of acrylic fibres, obtained from the DSC cell at 100°C/mi are shown in Fig. 1. The DTA curve for Acrilan (curve (d), Fig. 1.) should be co

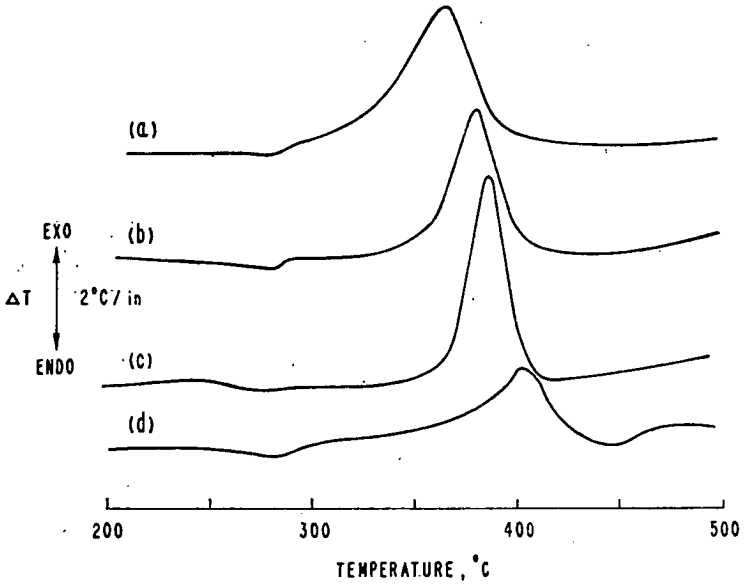
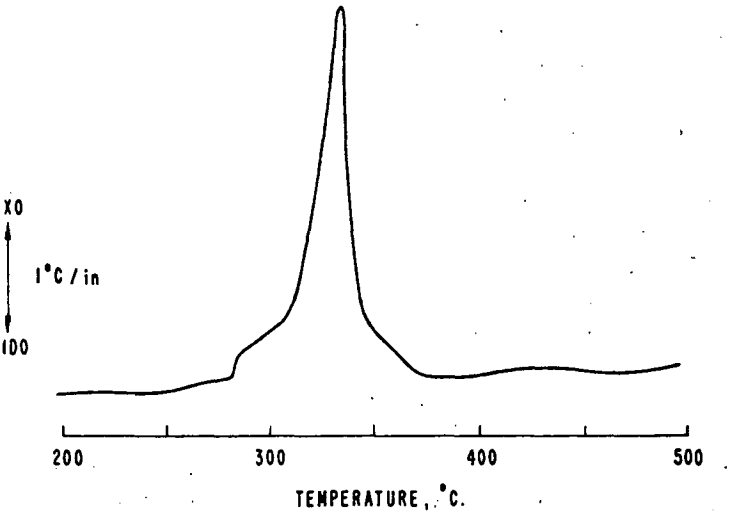


Fig. 1. DTA of acrylic fibres; (a) Orlon, (b) Cashmillon, (c) Creslan-61B, (d) Acrilan-16; enca sulated sample, DSC cell, heating rate, 100°C/min.

trasted with that obtained from the standard cell at 20°C/min (Fig. 2). Two effec contribute to the more positive identification of thermal events: the configuration the DSC cell[13] gives an improved baseline which is less subject to drift, and t procedural variables, as indicated above, improve the resolution of the exotherm decomposition. It should be noted that in the standard DTA cell, variation of samp preparation (weight and tightness of packing) can lead to the programmed heati rate being exceeded during the exothermic decomposition. Consequently the temper ture of maximum exothermic deflection is not reproducible in the standard ce However for the DSC cell at high heating rates both the shape of the thermogra and the temperatures of the thermal events were satisfactorily reproducible. In tho cases where determination of the melting point was possible at heating rates 20°C/min, good agreement was found between the value determined in the standa cell and that determined at the higher rate in the DSC cell. There was no differen between bright and semidull grades of the same fibre, due to the presence of a delustrant. It was not possible to distinguish between a low denier Courtelle tow a a much coarser grade of the same fibre.



2. Thermogram of Acrilan-16 fibre; sample in 2-mm tube, standard cell, heating rate 20°C/min.

Fig. 1 shows that the thermogram can be considered as three distinct regions; ing, exothermic decomposition, and post decomposition. The first two of these overlap. A fourth region, the glass temperature, would be expected between 60 100°C. For heating rates above 40°C/min it would be necessary to programme sample from subambient temperatures to establish an adequate baseline for ervation of the glass transition; however lower heating rates are preferable. le II lists the temperature at the onset of melting and of decomposition, as well as

LE II

ING AND DECOMPOSITION TEMPERATURE OF ACRYLIC FIBRES (DSC CELL AT 100°C/MIN)

	Major comonomer[16]	*Melting point* (°C, *Chromel–alumel*)		*Decomposition* (°C, *Chromel–alumel*)	
		T_0[a]	T_{max}[b]	T_0	T_{max}
		335	346	320	386
rtelle	6% Methyl acrylate	278	288	235	357
ian-16[c]	7.5% Vinyl acetate	255	284	[d]	400
nel-17[c]		250	284	[d]	394
n			280	260	362
millon		240	277	310	377
bel		230	277	310	377
an-61B[c]	10% Methyl Methacrylate	[e]	275	310	387
n-DK		230	275	[d]	385

iation temperature. [b]Temperature of maximum ΔT amplitude. [c]Identical thermograms for bright semifull grades of the fibre were obtained. [d]Decomposition begins during melting. [e]An exotherm eeds melting.

the temperature at maximum ΔT amplitude during these processes, for a series acrylic fibres. No tabulation of the postexothermic effects has been given, since tl are associated with terminal degradation of the material and are not sharply defin However the observed differences are useful in discriminating between the materi (Fig. 1).

The materials listed in Table II are arranged in order of decreasing melt point which has been found to correlate with the amount of the major copolyr present, where this has been reported[16]. The onset of melting of the Orlon sam (curve (a), Fig. 1) cannot be determined accurately because of the coincidental on of decomposition and the resultant smallness of the endotherm. In contrast the on of melting of Creslan (curve (c), Fig. 1) is obscured by an exotherm immediat before the melting point. This effect, which is shown only by Creslan could be due either reaction or to premelting crystallization.

Table II shows that, under conditions of fast heating rate, there are signific variations in the decomposition of these fibres. Thus, compared to the homopolym the copolymer containing vinyl acetate (COPAN, Acrilan) begins to decompose a lower temperature while the maximum ΔT amplitude occurs at a higher temperatu The presence of methyl methacrylate in the copolymer (Creslan) also results in earl decomposition but the position of maximum ΔT is unchanged, while for a copolyr containing methyl acrylate (Courtelle) both temperatures are much lower. Detai analysis of the decomposition is precluded by the limited information[16] available these commercial fibres. Indeed it should be noted that, whereas Von Illers[10] obser an increased stability of methyl acrylate copolymers compared to PAN, Courte with a similar reported copolymer content, showed a different relative stability. T may be attributed to differences in either the physical preparation of the samples, more probably, in the chemical composition and history of the materials.

A method for estimating the activation energy for the thermal decompositi of PAN by isothermal DTA has been described[12,15]. A value of 44 kcal·mol^{-1} v obtained. Similar studies on extracted COPAN yielded a value of 31 kcal·mol and show the effect of comonomer. In textile fibres the presence of finish oils effe both the definition and duration of the induction period before the exotherr decomposition and, to ensure comparability, these oils must be extracted from t fibre before determination of the activation energy for the reaction.

This constraint restricts the utility of this parameter in routine evaluation acrylic fibres; however determination of the activation energy for thermal decompc tion, together with the estimation of heat of fusion from the melting endother affords additional discrimination between acrylic fibres beyond that obtained fr simple qualitative evaluation of fast scanning rate DTA curves.

CONCLUSIONS

Results have been obtained from commercial materials of complex a undisclosed composition using fast heating rate DTA. Differences in the glass tran

point, melting point, and decomposition arise from the varying constitution of materials, and are disclosed by procedural comparisons based on the pattern of thermal events, relative peak positions, amplitudes and shapes. We believe that the technique may be usefully applied to the study of polyacrylonitriles of known composition and chemical and physical histories.

REFERENCES

1. W. DAVIS AND P. SHAPIRO, *Encyclopedia of Polymer Science and Technology*, Vol 1, Wiley, New York, 1964, p. 342.
2. K. KENNEDY, *Encyclopedia of Polymer Science and Technology*, Vol. 8, Wiley, New York, 1968, 812.
3. L. SMITH, *Encyclopedia of Polymer Science and Technology*, Vol. 6, Wiley, New York, 1967, 593.
4. BOURIET, *Bull. Inst. Textile Fr.*, 18 (1964) 397.
5. F. SCHWENKER AND R. K. ZUCCARELLO, *J. Polym. Sci. C*, 6 (1964) 1.
6. F. SCHWENKER, L. R. BECK AND R. K. ZUCCARELLO, *Amer. Dyestuff Rep.*, 53 (1964) 817.
7. T. TARIM AND D. M. CATES, *Appl. Polym. Symp.*, 2 (1966) 1.
8. F. SCHWENKER AND L. R. BECK, *Text. Res. J.*, 30 (1960) 624.
9. V. THOMPSON, *J. Polym. Sci. B.*, 4 (1966) 361.
10. -H. VON ILLERS, *Makromol. Chem.*, 124 (1969) 278.
11. E. SLADE, *Thermochim. Acta*, 1 (1970) 459.
12. DUNN AND B. C. ENNIS, *J. Appl. Polym. Sci.*, 14 (1970) 1795.
13. I. DUPONT DE NEMOURS & Co (Inc.), Instruments Products Division, Wilmington, Publication 0C.
14. . W. WENDLANDT, *Thermal Methods of Analysis*, Interscience, New York, 1964, p. 139.
15. N. HAY, *J. Polym. Sci. A1.*, 6 (1968) 2127.
16. SICLARI, in H. F. MARK, S. M. ATLAS AND E. CERNIA (Eds.), *Man Made Fibres: Science and echnology*, Vol. 1, Interscience, New York, 1967, p. 129.

Identification of transparent materials for safety applications

By
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Tough, optically clear materials such as toughened glass and plastics, are used extensively to provide a safety barrier between the eyes and face of the worker and his work and equipment (1, 2, 3, 4).

These barriers take a number of forms, ranging from individual goggles, safety spectacles, face visors and hoods to fixed transparent guards for machines and equipment.

These transparent materials differ widely in their properties, and recently the major advantages of plastics, such as light weight and good impact strength, have encouraged their use in safety devices. However, because they vary considerably in their resistance to solvents and their ability to withstand impact it is important that the correct material be specified, and used, in safety applications. Typical properties of some of these materials are given in Table 1.

Not only must the correct material be specified but care must be taken to ensure that the chosen one is supplied. Usually it is not possible to distinguish one material from another by simple visual inspection and the need exists for simple identification tests.

An identification scheme has been developed that will enable commonly used transparent materials to be identified using simple and standard equipment usually found in typical engineering workshops. Materials that can be identified include: toughened glass, laminated glass, polymethyl methacrylate (PMMA), polycarbonate, cast allyl plastics, cellulose acetate, cellulose propionate, rigid polyvinylchloride (PVC), polyvinylidene chloride and poly-4-methylpentene-1. This last transparent material has only recently been introduced, and, although not widely used yet, it has potential in safety devices.

Other less common plastics available in transparent form include epoxy resins, polyester resins, polystyrene, polystyrene-acrylonitrile copolymers, polystyrene-polymethyl-acrylate copolymers, polycarbonate blends, polyvinylidene fluoride and polychlorotrifluoroethylene (PCTFE). Special analytical techniques such as infra-red spectrophotometry and pyrolytic gas chromatography may be required to identify many of these materials.

The identification scheme developed for use with the materials listed in Table 1 is shown schematically in Figure 1.

Glass, toughened glass, and glass-polyvinyl butyral laminates may be distinguished from transparent plastics by virtue of their high surface hardness and their specific gravity. Thus all these glass materials cannot be scratched by a chisel point 6H pencil; however, all the transparent plastics are permanently scratched when tested in this way. The glass materials, with a specific gravity of 2.4 - 2.8, sink in liquid trichloroethylene (specific gravity, 1.48), while the plastic materials (specific gravity, 1.18 - 1.40) all float. Trichloroethylene as used in standard degreasing baths would be suitable for this test. With laminated glass materials, the type of construction is often visible on examination of the edge.

Of the transparent plastics, poly-4-methylpentene-1 (TPX) may be rapidly and simply identified by virtue of its low density (specific gravity, 0.83) which enables it to float in water. All the other transparent plastics (specific gravity, 1.18 - 1.40) will sink in water.

The behaviour of the various plastics materials when abraded by an emery or carborundum grinding wheel is also an excellent guide to the nature of the material. Cast allyl polymers, being thermosetting materials, are abraded away slowly giving no formation of swarf and a fine white powder residue. All the other transparent plastics being thermoplastics are softened and flow under the pressure and frictional heating and form a swarf in the area of

TABLE 1
Properties of Transparent Materials

Material	Typical Trade Names	Specific Gravity	Heat Distortion Temperature, °F* 66 psi	264 psi	Optical Properties: Transmission	Refractive Index	Impact Strength (Izod)** ft lb/in of notch	Solvent Resistance
Toughened glass	Various	2.4-2.8	—	—	Approx. 92%	1.52	—	Resistant to solvents.
Glass-Polyvinylbutyral laminate	'Bandit' glass Safety glass	Varies with laminate construction	—	—	Approx. 80%	Approx. 1.52	—	Resistant to solvents.
Poly-4-methylpentene-1	'TPX'	0.83	293	—	90%	1.47	0.8	Swollen by aromatic hydrocarbons, chlorinated carbons, etc. Not affected by ketones, alcohols and esters.
Polymethyl methacrylate (PMMA)	'Perspex','Diakon', 'Plexiglas', 'Lucite', 'Oroglas'	1.17-1.20	165-235	155-210	92%	1.48-1.50	0.4-0.5	Soluble in ketones, esters, aromatic hydrocarbons and chlorinated hydrocarbons.
Polycarbonate	'Lexan' 'Makrolon' 'Merlon'	1.20	285	265-280	90%	1.586	12-16***	Soluble in aromatic and chlorinated hydrocarbons. Softened and cracked by ketones and esters.
Cellulose acetate	'Tenite-I', 'Bexoid' 'Celsior' 'Cellidor A'	1.23-1.34	120-205	111-190	Approx. 90%	1.46-1.50	0.4-5.2	Soluble in ketones and esters. Softened or slightly soluble in alcohols. Not greatly affected by hydrocarbons.
Cellulose propionate	'Forticel'	1.18-1.24	158-250	111-228	Approx. 90%	1.46-1.49	0.5-11.5	As above.
Cast allyl resins	'Allymer CR-39' 'Armolite', 'Plastough' 'Homolite CR-39'	1.30-1.40	—	140-190	92%	1.50-1.57	0.2-0.4	Resistant to nearly all solvents.
Rigid Poly vinylchloride (PVC)	'Darvic' 'Cobex' 'Luvitherm'	1.35-1.40	179	130-164	Approx. 82%	1.52-1.55	0.4-2.0	Resists alcohols, aliphatic hydrocarbons and oils. Swollen by aromatics and ketones. Soluble in chlorinated hydrocarbons.

* ASTM Test Method D648
** ASTM Test Method D256
*** (¼ x ½ inch test specimen)

g. Some plastics depolymerize or
ose during severe abrasion and
our of the resultant products is
haracteristic. The fruity odour of
methacrylate derived from
can be used to distinguish this
polymer.
behaviour of certain transparent
in solvents is a good identifica-
t, and a 15 second immersion in
can enable some materials to
inguished. Cast allyl plastics are
ted while PMMA may show
urface crazing, and on drying the
ion of a white opaque deposit.
olycarbonate and the cellulosic
ls are softened sufficiently by the
for the surface to become tacky
ke a permanent thumb or finger
hen squeezed between the fingers
oderate pressure.
drying the polycarbonates develop
e opaque deposit after acetone
sion. This deposit does not form
cellulosic plastics. Polycarbonates
llulosics immersed in acetone (15
s) and then heated in boiling water
a cellular, friable surface due
rapid loss of absorbed solvent.
d PVC and polyvinylidene chloride
ly very slightly affected by a 15-
immersion in acetone and suffer
very slight loss of surface gloss.
chlorinated transparent plastics
and polyvinylidene chloride) may
ntified by the copper wire-flame
this test a copper wire is heated
heat in a gas or oxyacetylene
and whilst hot pressed into the
of the sample so that a small
t of molten plastic adheres to the
the wire. The wire is then re-
in the flame. With chlorinated
materials a green flame is ob-
an effect which does not occur
ne other plastics.
differences in the softening points
transparent plastics can also be
distinguish some materials. On
sion for five minutes in boiling
cellulose acetate and propionate
ftened so much that components
eform under their own weight.
mponents made from PMMA, PVC
olyvinylidene chloride are softened
ntly to be deformed by the
tion of a moderate force. Poly-
ates remain rigid after immersion
ing water. Cast allyl plastics are
ot grossly softened by boiling
but on flexing may break due to
ytic degradation.

Hardness testing of transparent plastics

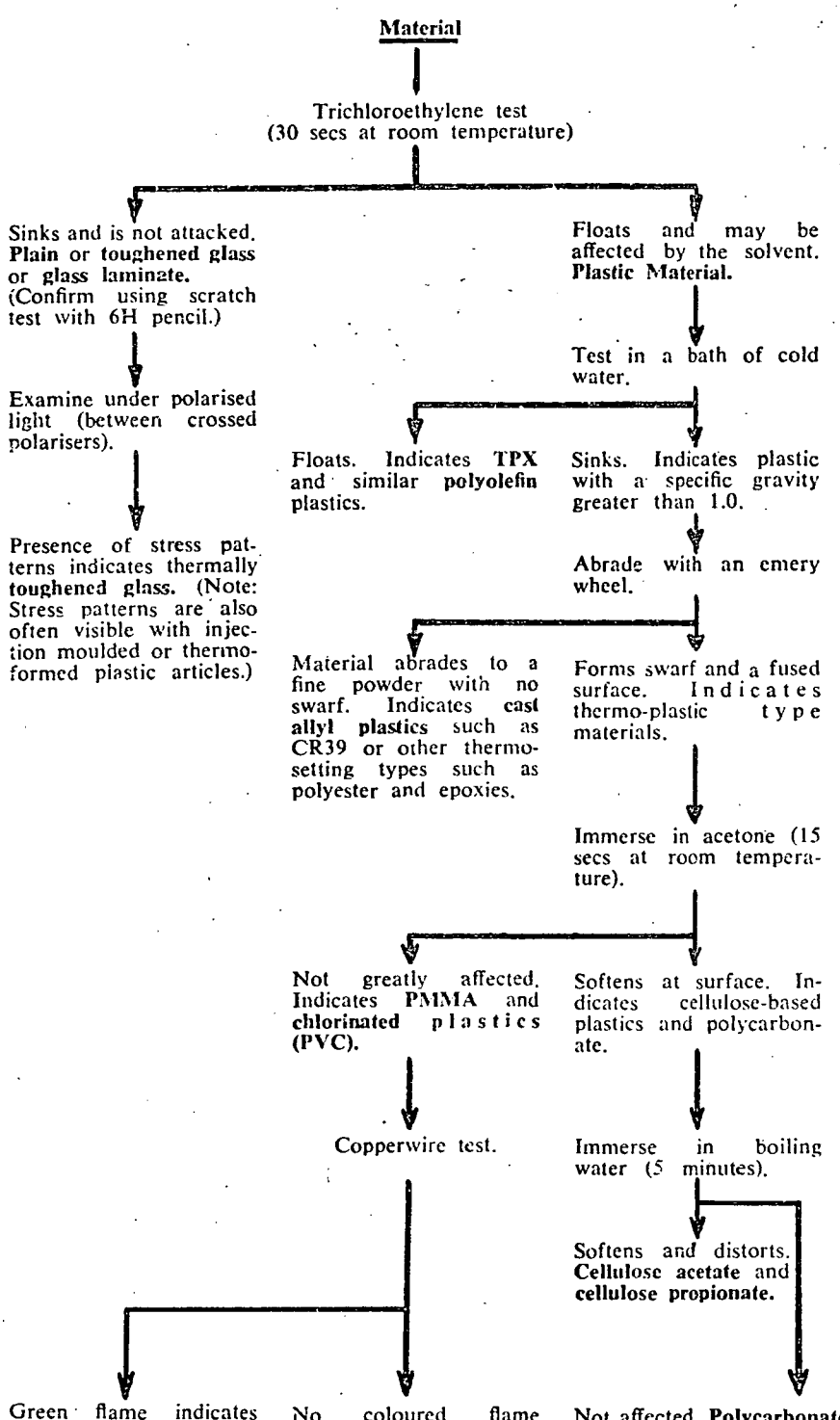
nsparent plastic materials may
e rapidly identified by use of the
Hardness Impressor (5). This
le tester (value about $120) is
nly used in workshops where
ced plastics such as polyester or
resins are processed. Although
nces in formulation and thickness
ch plastic may cause variations
dness over a range of 2-3 points,
erage figure is a good guide to
pe of plastic.
ical hardness values, determined
15 seconds, using two different
testers are given in Table 2.

Table 2

Hardness Values of Transparent Materials After 15 Seconds.

Material	Barcol Impressor Hardness Model GYZJ-934-1	GYZJ-935
.....	100	100
(type 8)	44-46	88-90
llyl resin	26-27	79-80
PVC	10-16	70-75
rbonate	14-16	70-72
-methylpentene-1	0	55-57
se acetate or se propionate . sticised)	0	55-57

Figure 1: Schematic diagram for the identification of transparent materials.



Surface impressions on plastics caused by the Barcol indentor can readily be detected by examining the transparent plastic under polarized light.

Conclusions

In order to protect workers during hazardous operations, transparent safety barriers are required. As well as specifying the correct material, it is important to ensure that the selected material is used. With the simple tests described above it is possible to identify transparent materials used in safety devices, using only equipment, techniques and materials which can be found in almost any workshop.

References

1. Anon. "The Spectral-Transmissive Properties of Plastics Used in Eye Protection." Sectional Committee Z2, United States of America Standards Institute, New York, NY (1955).

2. Keeney, A. H., "Lens Materials in the Prevention of Eye Injuries." Publication No 307, American Lectures in Ophthalmology, Charles C. Thomas, Publisher, Springfield, Ill (1957).

3. Woods, H., (Chairman) and others. "Report of the Joint Advisory Committee on Foundry Goggles." Ministry of Labour, Her Majesty's Stationery Office, London (1964).

4. British Standard 2092:1967, "Specification for Industrial Eye Protectors." British Standards Institution, London (1967).

5. ASTM D2583-67, "Test for Identification Hardness of Plastics by Means of a Barcol Impressor (Model 934-1)." American Society for Testing and Materials, Philadelphia, Pa (1967).

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APPENDIX 27 REVIEW ARTICLES

27a Organic Materials in Adverse Environments.
P. DUNN. Report 458
Defence Standards Laboratories,
Department of Supply, Melbourne
Australia 27.2 - 27.21

27b Polymers in Adverse Environments
P. DUNN
Proc. Roy. Aust. Chem. Inst., 40, 65 (1973) 27.22 - 27.27

DEPARTMENT OF SUPPLY
AUSTRALIAN DEFENCE SCIENTIFIC SERVICE
DEFENCE STANDARDS LABORATORIES

REPORT 458

ORGANIC MATERIALS IN ADVERSE ENVIRONMENTS

P. DUNN

SUMMARY

Organic materials, such as plastics, rubbers, adhesives, sealants, fabrics and paints, are now being developed for use in more and more adverse environments. As these materials gain greater market penetration in building construction, transportation, agriculture, packaging, furniture, and domestic appliances, an increased level of performance under a wide range of environmental conditions will be required.

The tropical deterioration of organic materials, the use of polymers underwater, the corrosive effects of organic materials, the stress cracking of organic materials and the flammability and smoke-producing properties of materials, are discussed. Information is presented on the selection of organic materials for particular applications, and conclusions drawn concerning major developments expected over the next few years.

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ORGANIC MATERIALS IN ADVERSE ENVIRONMENTS

1. INTRODUCTION

Modern military equipment makes extensive use of polymeric materials for a wide range of applications. The reasons for the selection of a rubber or plastics material for military items are often as varied as those which apply to the selection of materials for industrial or commercial applications. However factors such as weight saving and improved resistance to most forms of environmental degradation are of considerable importance.

During the Second World War, fighting on a large scale using modern technical equipment occurred under a wide range of environmental conditions. Equipment losses, failures and casualties directly due to adverse environments because of corrosion, microbiological attack, and actinic degradation, were enormous.

As a result, military planners throughout the world have realized that special investigation of the effects of adverse environments on materials, articles and entire systems is an important activity for any nation whose defence is based on modern aspects of technology. Australia is such a nation. In this paper we will describe some work undertaken in Australia to evaluate the performance of organic materials such as rubbers, plastics, and adhesives in adverse environments. The aim of this work is to be able to advise the Armed Services of the correct use and application of these materials in all types of military equipment. The effect of these organic materials on other materials and components of entire systems, will also be discussed.

2. DETERIORATION OF ORGANIC MATERIALS - GENERAL

Polymeric organic materials find a wide outlet in items based on rubbers, plastics, adhesives, sealants, textiles, films, fabrics, paints, coated fabrics, and metallized components. Polymers have always been recognised for their inherent resistance to many environments, and this has encouraged their use in a wide range of applications. Industries concerned with building construction, transportation, marine application, agriculture, packaging, electronics, furniture, luggage, toys, and domestic applications find increasing applications for all types of organic material. These new applications involve polymers which are subject to adverse environmental conditions such as chemical and biological attack, outdoor weathering, high and low temperatures and mechanical abuse.

The attractive properties of many organic materials encourage their utilization in applications where resistance to corrosion is required. Care is necessary in the selection of specific materials to ensure that the optimum characteristics and properties are obtained, and that the selected material will have a useful life compatible with that of the entire system.

3. TROPICAL DETERIORATION OF ORGANIC MATERIALS

Organic materials are susceptible to attack by fungi, bacteria, insects, and rodents as well as to degradation by ultraviolet radiation and other factors associated with weathering. The microbiological deterioration of rubbers and plastics has been reviewed comprehensively by Heap (1) and others (2, 3) while Pacitti (4) has reviewed the attack by insects, rodents and other agents. Recent books by Rosato and Schwartz (5, 6), the symposium report of Kamal (7) and the papers by Eshenaur (8) and Sansom (9) also give much useful data.

Every year much military equipment and materiel is damaged, destroyed or rendered unsafe as a result of microbiological attack. Organic materials such as plastics, rubbers, adhesives, paints, fuels, lubricants, textiles and foodstuffs are all susceptible to deterioration by fungi. However modifications to formulations can reduce the ability of fungi to survive on many organic materials.

All the factors causing the deterioration of materials are not known, so while it is possible to carry out laboratory testing in order to assess some effects such as temperature, humidity, fungal and bacterial attack, artificial ageing, attack by ozone etc., it is still necessary to undertake outdoor exposure tests in areas where the environment can be described as adverse. The establishment of Joint Tropical Research Unit (JTRU), Department of Supply at Innisfail, North Queensland in 1962, enabled field exposure trials on organic materials to be carried out under supervision. The sites of JTRU were selected in order that the effects of the different environments on materials of interest, could be studied. Typical meteorological data for the three main JTRU exposure sites and for Melbourne, over a five-year period, are given in Table 1.

Since the Unit commenced operations, eight years ago, over fifty exposure and storage trials have been commenced on a range of materials. Typical aims of these trials have been to determine the resistance of a wide range of plastics to degradation by ultraviolet radiation, the resistance of adhesive-bonded metals to "hot-wet" and "hot-dry" conditions, the resistance of paints to weathering, the ageing characteristics of rubbers in "hot-wet" and "hot-dry" storage, the resistance of certain plastics to fungal attack, and the resistance of coated and/or impregnated timber to attack by marine boring organisms. As expected, a large number of all the trials being undertaken at JTRU are concerned with organic polymeric materials in some form or another.

Weathering is the result of six separate, yet inter-related variables, which are:- temperature, relative humidity, total precipitation, wind speed and duration, radiation and chemicals in the air, including natural chemical components and pollutants. Weathering is mainly a photo-oxidation process, which leads to discolouration and loss of strength due to embrittlement. This latter factor is the result of chain scission, cross-linking, or both, and is the direct cause of mechanical failure. As most degradation due to weathering is dependent on oxygen concentration at the reaction site, either on or within a polymer, the morphology,

composition and form of the material being evaluated, is of importance. Most polymers are damaged to some degree by ultraviolet radiation and thus depending on their chemical structure, polymers have varying degrees of resistance to weathering.

Polymers most resistant to weathering are poly(methyl methacrylate) and fluorine-containing materials. Polymers with poor resistance to weathering include unprotected polyolefins, polyacetals, poly(vinyl chlorides) and polystyrenes. Although these base polymers have, in many instances, poor weathering characteristics, proper modification of the polymer itself, as well as suitable formulating can markedly improve performance. Typical polymer structures shown in Figure 1, show increasing resistance to weathering in the order, polyethylene, poly(vinyl chloride), poly(vinylidene chloride) and polytetrafluoroethylene. As a general rule aromatic polymers are more stable than aliphatic polymers, and substitution of the aromatic ring, increases stability even further. Saturated polymers are more stable than unsaturated polymers, small molecules are usually stable, and linear chains are more stable than branched chains. These factors need to be considered when selecting polymers for special outdoor applications.

As an example, the outdoor weathering of polyolefins gives an indication of the severity of outdoor weathering in the Australian environment and of the use of special pigments such as carbon black to give increased protection.

Prolonged trials with a range of polyolefins has confirmed the efficiency of carbon black pigmentation as a suitable means of protecting these materials against photo-oxidation. The results shown in Table 2 indicate how carbon black-pigmented and natural polyolefins performed at the various exposure sites in Australia. The effect of different exposure sites on the mechanical properties of low-density polyethylene, is shown in Figure 2. At "open" sites at JTRU, Cloncurry and Innisfail the loss in tensile strength was most marked, while for specimens exposed in the "jungle", the change in tensile strength was almost insignificant. These results confirmed the importance of ultraviolet radiation as the primary cause of deterioration of unprotected polyolefins. The effect of stress in polyolefin mouldings as a result of processing conditions is also of considerable importance. As shown in Figure 3, severe cracking due to weathering can occur along lines of stress. Stress-free specimens should exhibit improved weathering characteristics.

To obtain the best outdoor performance from the polyolefins, as indeed with most of the thermoplastics, it is necessary to use carbon black pigmentation. Details of outdoor weathering trials undertaken on polyolefins (10), on plasticized poly(vinyl chloride) (11) and on some ethylene-propylene terpolymer rubbers (12), are available.

4. POLYMERS FOR UNDERWATER APPLICATIONS

Organic materials in the form of surface coatings, hot-melt coatings or heavy duty sheetings are widely used to give protection to ships and underwater structures against corrosion due to fresh water and to seawater. These same coatings can also be used to protect timbers in underwater locations from attack by marine organisms.

On behalf of Navy, a trial has been conducted at Clump Point, North Queensland, on the development of suitable coatings for the protection of timber immersed in seawater, against marine boring organisms. A typical example of borer penetration into coated Khaya invorensis (West African mahogany) panels after immersion for one year, is shown in Figure 4. Coatings for evaluation include reinforced and unreinforced epoxy and polyester resins, acrylic emulsions, poly(vinyl chloride) and polychloroprene and chlorosulphonated polyethylene rubbers. Some of the panels, and also their coatings contained organic biotoxins in order to reduce attack by marine borers and the effect of the other marine fouling organisms. Panels impregnated with organotin compounds and coated with a number of coatings showed good resistance to marine borers and some resistance to marine fouling. Trials of this type have been in progress for three years and are continuing. Four types of organic coatings have shown exceptional resistance to attack by marine boring organisms. We are also continuing to investigate the use of organotin compounds as additives for rubbers and plastics, in an attempt to develop materials with special characteristics. Typical materials of interest have recently been described by Evans (13).

5. CORROSIVE EFFECTS OF ORGANIC MATERIALS

Although polymers are generally considered to be inert materials, corrosion problems can arise if they are used incorrectly. The corrosion of metals in equipment is influenced by volatile products arising from other materials which may also be present. Plastics, rubbers, foams and wood can be a source of such products. Even when no volatile materials are present, corrosion of a metal can occur from contact with some organic materials.

The corrosion of metals by organic materials is of considerable importance in electrical equipment, and the book by Rychtera and Bartakova (14) reviews the subject in detail. The corrosive effect of plastics, rubbers and wood on metals in confined spaces has also been reported by Knotkova-Cermakova and Vlckova (15). As well as the polymer itself, compounding ingredients used in formulations for rubbers and plastics can create serious corrosion problems. Chlorinated compounds used as flame retardants for poly(vinyl chloride) can be very corrosive, while sulphur compounds used as vulcanizing agents for rubbers can cause serious staining of silver and other metals. Specifications are available (16) to control the quality of special non-silver staining rubbers used in close proximity to electrical equipment. Blowing agents used in the production of expanded rubbers can produce highly alkaline materials, which can induce corrosion in some metals. Alkaline amine vapours can also be produced from some

polyurethane rigid and flexible foams. Polystyrene foam which is widely used in packaging applications is produced by expansion of polystyrene beads, using steam. The water content of freshly expanded material is often around 5%, and unless this is reduced to below 0.5% by air or oven drying, before use, serious corrosion problems can occur.

The interest in carbon fibres as high performance reinforcing materials is exemplified by the scope of papers presented at a recent international conference (17). A major disadvantage (18) of these materials in their use in contact with light alloys, could be the corrosion hazard of the combination. Carbon fibre reinforced plastics have an electrochemical potential of about + 0.4 V while aluminium alloy has a value of about - 0.7 V, with respect to the hydrogen electrode. In combination therefore they will be subject to corrosion in the presence of an electrolyte. To prevent this, metals such as stainless steel, titanium or nickel may need to be used, or alternatively the two materials would need to be insulated from each other.

In the building and transportation industries especially, poly(vinyl chloride) (PVC) is extensively used, and in Australia at present PVC is beginning to seriously challenge traditional materials used in plumbing and electrical applications (19). While PVC does not burn readily, it decomposes at relatively low temperatures to give toxic and corrosive products (20, 21). The proportion of time at a recent symposium (22) devoted to this plastic reflects the concern with which this aspect of PVC technology is regarded. We (23) have also studied the thermal decomposition of PVC, and shown that the rate of decomposition and dehydrochlorination can be greatly affected by the type and quantity of plasticizer and stabilizer present. As the thermal decomposition of PVC results in the liberation of large quantities of hydrogen chloride, the corrosive nature of these decomposition products can create serious problems in areas where fires involving PVC, might occur.

6. STRESS CRACKING OF POLYMERS

Where premature failure of a polymer occurs in the presence of stress and an adverse environment together, then failure is known as environmental stress cracking. Rosen (24) has described typical fracture processes in polymeric materials, including stress cracking.

At Defence Standards Laboratories we have studied the stress cracking of polyamides (nylons) by a range of metal salts, including halides, thiocyanates (25) and nitrates (26). Although many organic polymeric materials are affected by organic solvents, the rupture of nylons by inorganic chemicals, was unusual. Nylons are also often used in many industrial applications where they could be in contact with metal salts which could result in serious failures.

Many metal halides and halide-like salts were found to be active stress-cracking agents, while metal acetates and sulphates were inactive.

Salts of zinc, calcium and lithium were found to be active stress-cracking reagents. The rupture of nylons by these agents was found to be dependent on temperature, moisture content of the nylon, concentration of the cracking agent and level of stress. High values of all these, favoured rapid cracking. Metal halides did not appear to cause chain scission in the nylon and stress cracking was not due to hydrolysis or to metal-ion catalysed hydrolysis.

Two types of changes were observed, depending on the metal halide involved, and on this basis the metal halides were classified as Type I or Type II. Type I metal halides, such as zinc, cobalt, copper and manganese chlorides form complexes in which the metal atom is coordinately bonded to the carbonyl oxygen atom of the amide group of the nylon. These agents cause stress cracking by interference with the hydrogen bonding in the nylon. Type II metal halides, such as lithium, calcium and magnesium chlorides and lithium bromide in solution form proton donating, solvated, species which act as direct solvents for nylon 6 in a manner similar to phenols and formic acid. Type II agents appear to cause simple solvent cracking.

All nylons absorb water to some degree, and the equilibrium water content was found to have a significant effect on the rate of cracking of nylons by metal salts. Where the water content is greater than 1-2% by weight, a serious stres-cracking hazard in nylon can exist. Moulded specimens of different types of nylons, were exposed in the jungle at JTRU and the water uptake over a period of several months, determined. The results, shown in Figure 5 indicate that only nylon 11 (polyundecanoamide) has an equilibrium moisture content under field conditions, of less than 2%. Practical experience has confirmed that this type of nylon, together with nylon 12, is generally resistant to stress rupture by metal salts.

The importance of corrosion fatigue in the breakdown of metal and non-metallic materials is confirmed by the scope of a recent international conference held on the subject (27). Subjects such as:- corrosion fatigue of rubber in several hostile environments, crazing and cracking of thermoplastics in organic media, corrosion fatigue of plastics in organic media, environmental stress corrosion cracking of glass and environmental stress cracking of glass fibre reinforced thermoplastics, were discussed in detail.

In the selection of a plastics, rubber, adhesive or surface coating for a particular application, care is necessary to ensure that the chemical resistance of the material is adequate for the intended application. The Rubber and Plastics Research Association of Great Britain, has recently commenced the issue of a series of data sheets, detailing the chemical resistance properties of a wide range of rubbers and plastics (28), while the paper by Peters (29) gives comparative data of 55 polymers against 320 chemicals and other environments.

7. FLAMMABILITY OF ORGANIC MATERIALS

The increased utilization of polymers in the building and transportation industries, has stimulated research and development aimed at reducing the flammability and smoke-producing properties of a wide range of organic materials. As many of these materials are used to give protection against corrosion, or to provide a decorative finish to components based on steel, stone or concrete, it is essential that materials with a high degree of flame resistance be used. A new scientific journal primarily devoted to this subject has recently appeared (30).

Although some polymers such as poly(vinylidene chloride), polytetrafluoroethylene etc., have good flame resistance, other polymers need to be modified by formulating, in order to impart an acceptable degree of resistance. Fillers containing bromine, chlorine, antimony and phosphorus are widely used in selected combinations aimed at producing synergistic effects. Hydrated alumina, which is a satisfactory flame retardant for phenolic and polyester resins, is claimed to be effective because the water of hydration associated with the alumina acts as a heat sink (31). In a fire situation, the products of combustion of fire-retardant organic materials can be very corrosive and special precautions may be needed to reduce possible secondary damage.

New techniques have recently been developed to assess the flammability and smoke-producing properties of organic materials. The General Electric Flammability Index Tester (32-35) is a device which determines the relative flammability of materials by a very sensitive and reproducible technique. Unlike most traditional measures of flammability, the G.E. technique depends on a variable which can be measured precisely - the minimum volume concentration of oxygen required to support the combustion of a material sample. This minimum value is described as the limiting oxygen index and can be determined to an accuracy of less than one percent of the index.

A small material sample is clamped upright inside a vertical glass chimney, ignited at the top and allowed to burn in a candle-like manner. The flammability is determined by adjusting the concentration of gases (oxygen and nitrogen) rising past the sample by means of an accurate gas metering unit.

The G.E. Tester correlates with the test specified in Underwriters Laboratories Bulletin 94. For "self-extinguishing materials" as described in the Underwriters Laboratories procedure, the Oxygen Index is equal to or greater than 27% (34). The technique has recently been adopted as ASTM D-2863 (36) for use with plastics.

The oxygen index ratings of some typical polymers are:-

Material	Oxygen Index
Poly(methyl methacrylate)	0.173
Polystyrene	0.183
ABS/Polycarbonate alloy	0.202 (air equivalent)
Nylon 66	0.287
Poly(vinylidene chloride)	0.600
PTFE	0.950

Smoke generation from burning organic materials can be determined using the Rohm and Haas XP2 Smoke Density Test Chamber. The smoke chamber is a cabinet measuring 30 inches high, 12 inches wide, and 12 inches deep, completely enclosed except for 1 inch high ventilating openings round the bottom (37-40). The heat source is a propane-air flame from a pencil tip burner, applied at a 45-degree angle to the bottom of a horizontal specimen. A horizontal photometer path, 20 inches above the bottom of the chamber, is used for measuring light absorption.

The test chamber is used for measuring and observing the relative amounts of smoke produced by the burning or decomposition of plastics. Smoke producing characteristics of plastics are measured under controlled conditions of combustion or decomposition. The measurements are made in terms of the loss in light transmission through a collected volume of smoke produced under controlled, standardized conditions and may be used for evaluating smoke produced by wood, paper, fabrics and other organic materials. The apparatus has recently been adopted as ASTM D-2843T (41), for use with plastics.

By evaluation techniques such as these it should be possible to reduce the flammability and smoke-producing properties of organic materials used in a wide range of critical applications. Buildings, vehicles and consumer products with improved safety features should thus be possible.

8. CONCLUSIONS

As polymeric organic materials of all types become more widely used in military, industrial and consumer applications, they will be required to perform satisfactorily in a wide range of adverse environments. Plastics, rubbers, adhesives, textiles, coated fabrics, sealants, and paints will be developed with improved resistance to low and high temperatures, to organic and inorganic chemicals, to biological attack of all types, to weathering, and to severe conditions of mechanical abuse.

These improvements in overall performance will be achieved by variations in the morphology of the basic polymer system, by improvements in processing techniques to enable components to be produced with optimum chemical, physical and mechanical properties, by chemical modification of

the polymer, by the use of improved stabilizer systems, and by the development of better fillers and reinforcing materials.

Polymers with a high degree of resistance to flame and with associated low level of production of smoke on burning will be developed by chemical modification of the basic high molecular weight polymeric structure. This development should result in a reduced need for special additives to impart flame resistance to polymers which are known to be flammable. Associated problems associated with toxic or corrosive combustion products should also be reduced.

A basic understanding of all the factors associated with outdoor weathering of polymeric organic materials, will enable new plastics, rubbers, adhesives and paints to be developed, which will have service lives compatible with those of other materials. Materials should be available that will enable metallic substrates to be protected from corrosion and other forms of environmental deterioration, for the life of the whole system.

To achieve this however, it will be essential that the most suitable organic material for a particular application is selected and properly used. The need for chemists, physicists and engineers adequately trained in materials science is evident and necessary, if we are to gain the maximum advantage of the organic materials available now and the expected new range of sophisticated materials to be developed over the next few years.

9. ACKNOWLEDGEMENTS

The assistance of colleagues at Defence Standards Laboratories in undertaking some of the original work described, is acknowledged.

10. REFERENCES

1. Heap, W.M., "Microbiological Deterioration of Rubbers and Plastics". Rubber and Plastics Research Association of Great Britain. Information Circular No. 476 (1965).

2. MacLachlan, J., Heap, W.M., and Pacitti, J., "Attack of Bacteria and Fungi on Rubbers and Plastics in the Tropics - A Literature Review". Monograph No. 23, "Microbiological Deterioration in the Tropics". Society of Chemical Industry, London, p.185 (1966).

3. Anon, "The Attack of Rubbers and Plastics by Bacteria, Fungi and Insects, and Methods of Prevention". Bibliography No. 67, Division of Rubber Chemistry, American Chemical Society, Akron, Ohio (1966).

4. Pacitti, J., "Attack by Insects and Rodents on Rubber and Plastics", Rubber and Plastics Research Association of Great Britain, Shawbury, Information Circular No. 475 (1965).

5. Rosato, D.V., and Schwartz, R.T., "Environmental Effects on Polymeric Materials". Vol. 1 "Environments". Interscience Publishers, New York (1968).

6. Rosato, D.V., and Schwartz, R.T., "Environmental Effects on Polymeric Materials". Vol. 2 "Materials". Interscience Publishers, New York (1968).

7. Kamal, M.R., "Weatherability of Plastics Materials", Applied Polymer Symposia, No. 4, Interscience Publishers, New York (1967).

8. Eshenaur, R.E., Plast. and Polym. 37, 401 (1969).

9. Sansom, G.F., "Evaluation and Environmental Performance of Plastics Materials and Mouldings". Defence Standards Laboratories, Maribyrnong, Victoria. Report No. 309 (1970).

10. Dunn, P., and Hill, E.J., "Weathering of Polyolefins". Defence Standards Laboratories, Maribyrnong, Victoria. Report No. 421 (1971).

11. Dunn, P., Oldfield, D., and Stacewicz, R.H., J. Appl. Poly. Sci., 14, 2107 (1970).

12. Dunn, P., and Hart, S.J., Journal of the IRI, 3, No. 2, 81 (1969).

13. Evans, C.J., Tin and Its Uses. No. 88, 7 (1971).

14. Rychtera, M., and Bartakova, B., "Tropicproofing Electric Equipment". Leonard Hill (Books) Ltd., London (1963).

15. Knotkova-Cermakova, D., and Vlckova, J., Br. Corros. J. 6, 17 (1971).

16. British Standard 3106:1959, "Non-silver-staining Rubber Compounds". British Standards Institution.

17. International Conference on Carbon Fibres, their Composites and Applications. Preprints. The Plastics Institute, London (1971).

18. Corney, N.S., "A Review of Recent Advances in Carbon Fibre Technology, Carbon Fibre Composites and their Applications". Paper presented at the Symposium on Modern Ceramics and Ceramic Fibre Composites in Defence Applications". Canberra. April (1971).

19. "Plastics in Plumbing". Plastics News. The Plastics Institute of Australia. May (1971).

20. Boettnor, E.A., Ball, G., and Weiss, B., J. Appl. Polym. Sci. 13, 377 (1969).

21. Tsuchiya, Y., and Sumi, K.J., Appl. Chem., 17, 364 (1967).

22. SKYDD69. "Plastics - Fire - Corrosion". International Symposium on Corrosion Risks in Connection with Fire in Plastics. Sponsored by Research Foundation of the Swedish Fire Insurance Companies. Stockholm, April (1969).

23. Dunn, P., and Ennis, B.C., J. Appl. Polym. Sci. 14, 355 (1970).

24. Rosen, B., Editor, "Fracture Processes in Polymeric Solids - Phenomena and Theory". Interscience Publishers Inc. London (1964).

25. Dunn, P., and Sansom, G.F., J. Appl. Polym. Sci.,13, 1641 (1969).

26. Dunn, P., and Sansom, G.F., J. Appl. Polym. Sci., 14, 1799 (1970).

27. International Conference on Corrosion Fatigue. National Association of Corrosion Engineers. June 14-18. The University of Connecticut, Storrs. Connecticut (1971).

28. Butt, L.T., Pacitti, J., and Scott, J.R., "Chemical Resistance Data Sheets". Rubber and Plastics Research Association. Shropshire, England (1969).

29. Peters, R.L., "Environmental Rating of Plastics". Design News, Detroit (1967).

30. Journal of Fire and Flammability. Technomic Publishing Co., Stamford, USA. Vol. 1, 1970.

31. Holderried, J.A., Flame Retardants. Modern Plastics Encyclopedia (1968).

32. Fenimore, C.P., and Martin, F.J., Combustion and Flame, 10, 135 (1966).

33. Goldblum, K.B., SPE Journal, 25, 50 (1969).

34. Fenimore, C.P., and Martin, F.J., Modern Plastics, 44, 141 (1966).

35. Isaacs, J.L., J. Fire and Flammability, 1, 36 (1970).

36. ASTM D-2863, "Flammability of Plastics using the Oxygen Index Method". American Society of Testing and Materials.

37. Rohm and Haas Co., A Method of Measuring Smoke Density, N.F.P.A. Quarterly, 57, 276 (1964).

38. Hilado, C.J., J. Fire and Flammability, 1, 217 (1970).

39. Rarig, F.J., and Baristoc, A.J., "Evaluation of the XP2 Smoke Density Test Chamber. ASTM Special Technical Publication 422 (1967).

40. Gaskill, J.R., J. Fire and Flammability, 1, 183 (1970).

41. ASTM D-2843T, "Measuring the Density of Smoke from Burning or Decomposition of Plastics". American Society of Testing and Materials.

TABLE 1 - METEOROLOGICAL SUMMARY FOR EXPOSURE SITES

Period Jan 1963 - Dec 1968

	Melbourne	Innisfail, "Open"	Innisfail, "Jungle"	Cloncurry
Temperature, ^{o}F				
Highest daily max	111	104	97	113
Average daily max	68	82	78	91
Average daily mean (Note 1)	59	74	72	78
Average daily min	51	66	66	66
Lowest daily min	29	44	44	39
Relative Humidity, %				
Highest daily max	100	100	100	100
Average daily max	87*	94	97	52
Average Index of mean RH. (Note 2)	55*	82	90	37
Average daily min	28*	58	75	23
Lowest daily min	7	4	10	1
Percentage of time above 70% RH	-	79	92	8
Percentage of time below 60% RH	-	11	4	86
Precipitation				
Total rainfall, (ins)	141	775	-	79
Highest daily rainfall, (ins)	4.25	15.7	-	4.3
No. of rain days	848	1138	-	244
Duration of rain, (hours)	-	3740	-	406
Radiation				
Total sun hours (Campbell-Stokes)	12970	14940	-	21050

Note 1 : The daily mean temperature is taken as the mean of the daily maximum and daily minimum temperatures.

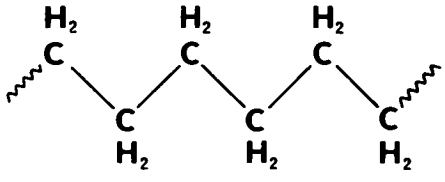
Note 2 : The average index of mean RH is derived from the ratio of the average 9 a.m. vapour pressure to the saturation vapour pressure at the average mean temperature (Note 1). Being thus related to the mean temperature this value of relative humidity is a good approximation of the daily mean.

* Mean relative humidity measured at 1500 h.

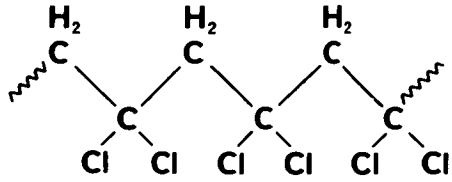
TABLE 2 - TENSILE STRENGTH OF EXPOSED POLYOLEFINS

MATERIAL Specimen, 0.10 in thick	UNEXPOSED	ULTIMATE TENSILE STRENGTH, PSI					
		1 YEAR		2 YEAR		3 YEAR	
		C[a]	I[b]	C	I	C	I
Polypropylene							
Natural	6180	F[c]	1640	F	F	F	F
Black	6130	6150	6120	6110	6110	5810	6000
HD Polyethylene							
Natural	3580	1330	1520	F	1080	F	625
Black	3790	3780	3780	3850	3770	3720	3770
LD Polyethylene							
Natural	2160	1230	1740	610	860	285	490
Black	2210	2240	2170	2300	2300	2340	2250
HD - LD PE Blends							
Natural	2280	810	780	F	430	F	F
Black	2450	2550	2450	2550	2460	2500	2460
PE Copolymer							
Natural	1500	800	950	250	410	F	290
Black	1920	1890	1900	2010	2050	1970	1930

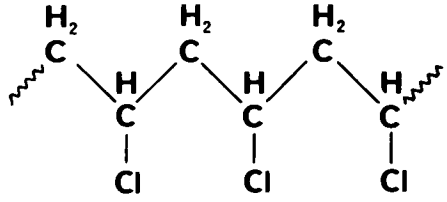
(a) Site C, Cloncurry "Hot-dry"
(b) Site I, Innisfail "hot-wet", "Open"
(c) F, Failed before testing



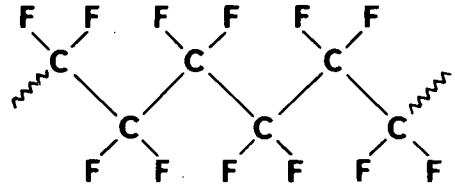
POLYETHYLENE



POLY(VINYLIDENE CHLORIDE)



POLY(VINYL CHLORIDE)



POLYTETRAFLUOROETHYLENE

Figure 1. Structures of some aliphatic polymers.

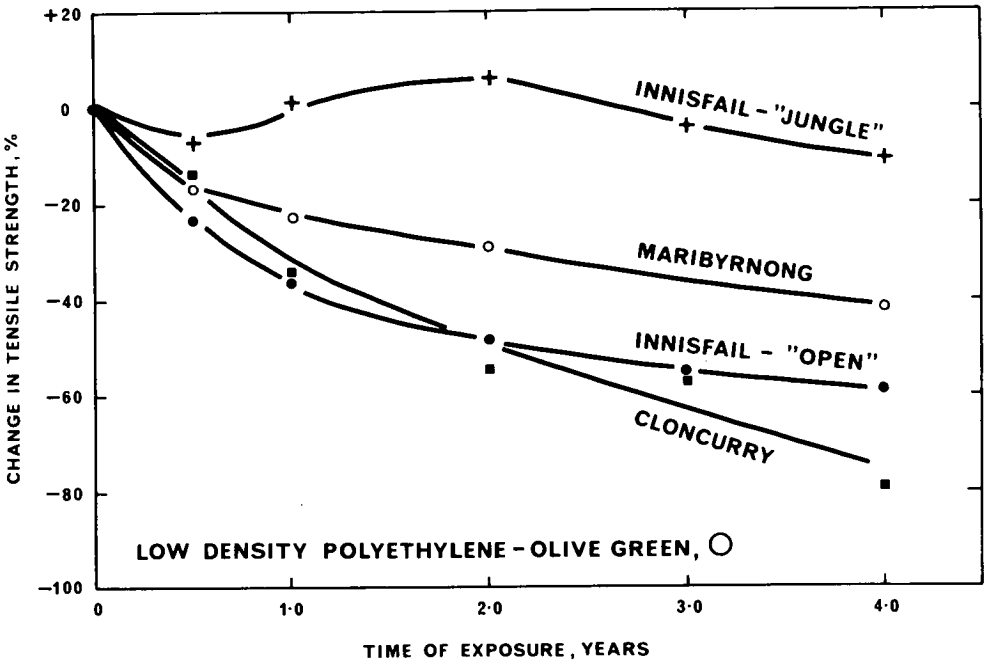


Figure 2. Relationship between change in tensile strength and time of exposure for low-density, olive-green polyethylene, exposed at four different sites.

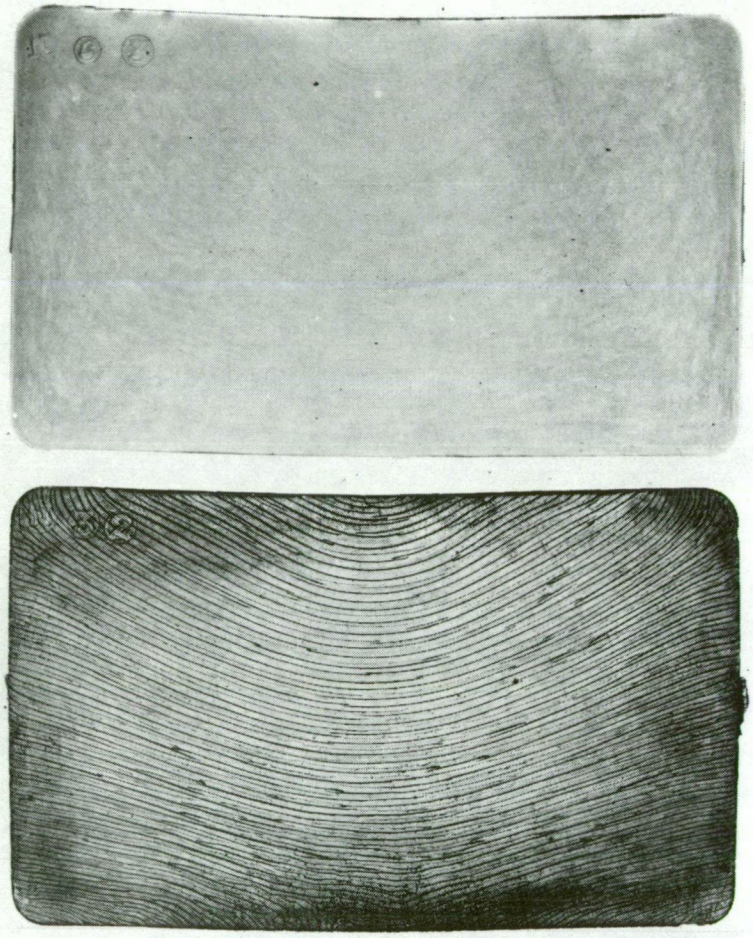


Figure 3. Specimens of low-density, unpigmented, polyethylene (N) before and after exposure at Maribyrnong for four(4) years. The weathered specimen (bottom) shows severe cracking, which has occurred along stress lines, induced during the injection moulding of the specimen. The stress pattern can easily be seen by viewing the unexposed specimen (top) with strong transmitted white light.

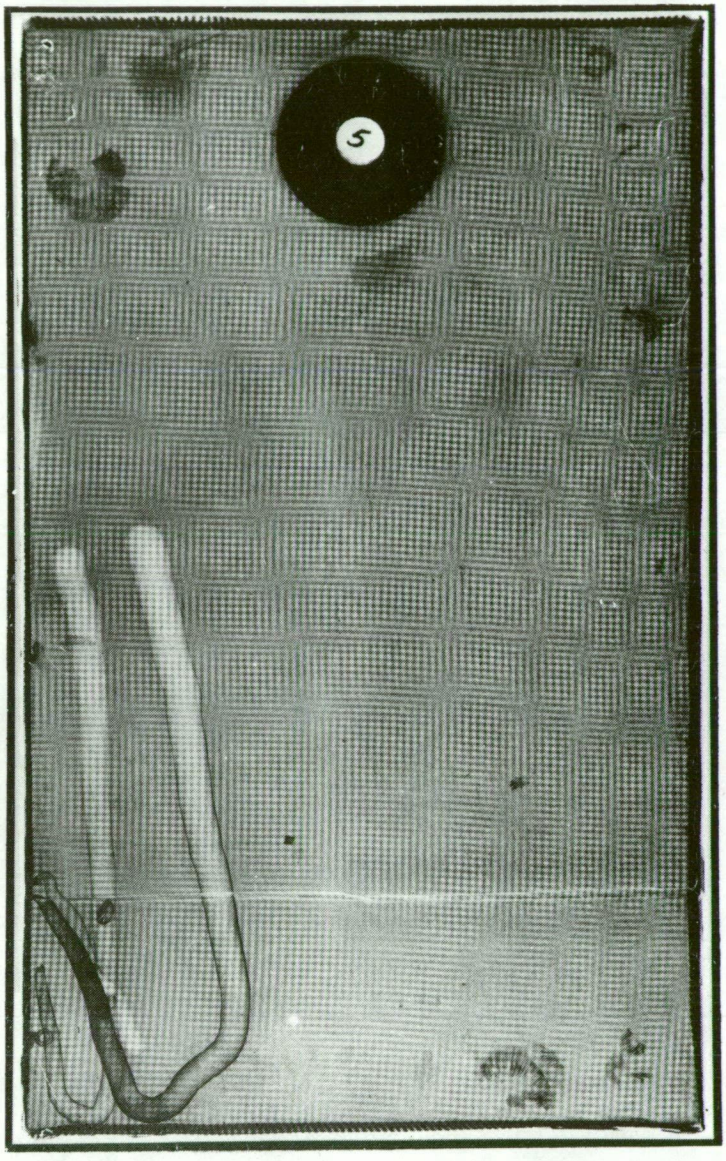


Figure 4. X-ray photograph of a timber panel coated with epoxy resin reinforced with fibreglass cloth, after immersion in seawater for one year. The tunnels made by borers, which penetrated the panel at the edge. can easily be seen.

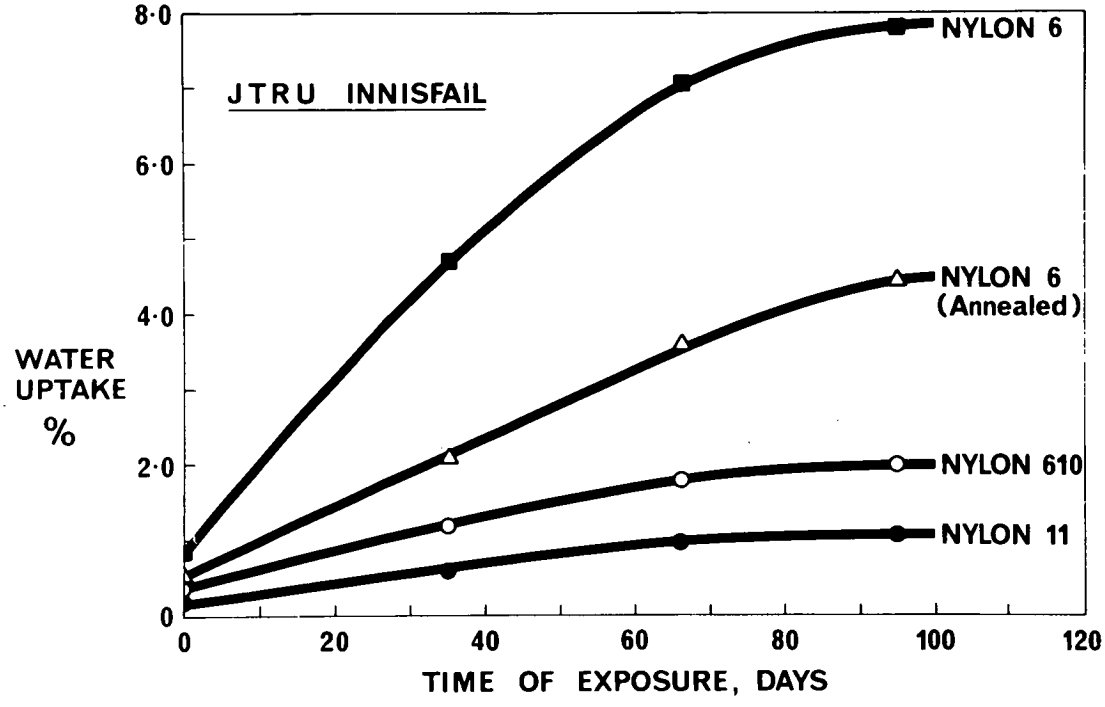
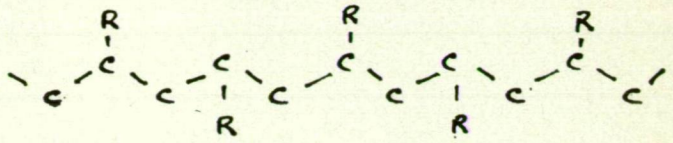


Figure 5. Relationship between water uptake of nylons and time of exposure, for specimens exposed in the "jungle" at JTRU, Innisfail.

POLYMER TOPICS



This feature, published on behalf of the Polymer Division, briefly surveys current thinking on aspects of polymer science. The articles, which are intended to be of general as well as specialist interest, are contributed by guest authors under the general direction of Dr. B. A. Bolto. Relevant comment and suggestions may be addressed direct to Dr. Bolto, C/o CSIRO Division of Applied Chemistry, Box 4331, G.P.O., Melbourne, Vic. 3001.

Polymers in Adverse Environments*

Contributed by P. DUNN, *Associate,* Defence Standards Laboratories, Maribyrnong, Victoria.

History shows that the development of most military equipment is evolutionary and that, with perhaps some isolated exceptions, this is not expected to change. To a certain extent, this development is associated with the availability of appropriate materials, whether they be metallic, ceramic or organic, coupled with the design information needed to exploit their particular characteristics. The introduction of phenolic, polystyrene and acrylic-type plastics, nylon fibres and to a limited extent some speciality synthetic rubbers just prior to World War II, marked the beginning of the use of man-made, organic polymeric materials. Before this time, most polymeric materials were based on natural products, for example, wool, cotton, silk, natural rubber, natural resins, gelatin, shellac, vegetable oils, etc. During the 1939-45 period shortages of strategic materials accelerated the development of polymeric materials such as synthetic rubber, polyethylene, poly(vinyl chloride), fluorinated plastics and speciality adhesives.

Developments initiated for military uses were exploited in the period after 1945 for commercial reasons. Intense industrial research and development activities during the period 1945-65 resulted in the introduction of a vast range of new synthetic polymeric materials including fluorinated rubbers, silicone rubbers, polyesters, polypropylene and high density polyethylene, polycarbonates, poly(phenylene oxides) and other 'engineering-type' plastics. In recent years the rate of development of new types of polymers has slackened, and greater emphasis has been placed on the improvement of well-established polymers and the development of special polymer alloys and blends. This trend is expected to continue.

* Based on a lecture given on 12 September, 1972, to the Victorian Branch Polymer Group.

Utilization of Organic Materials

Improvement in the chemical and physical properties of polymeric materials, for example, elastomers, plastics, foams, films, coatings, adhesives, and synthetic fibres, will depend on a better understanding of the relationship between molecular structure and properties as well as on new methods of synthesizing the necessary polymers. This will guide more successful tailoring of monomers, co-monomers, and polymerization conditions to attain desired properties.

The military forces utilize polymers in many diverse applications such as binders for solid propellants; insulation for electronic devices and jacketing for wire;

Mr. Dunn, a graduate of the University of Tasmania, has been with Defence Standards Laboratories, Department of Supply, Maribyrnong, since 1951. Initially he worked in the field of toxic organic chemicals and about 1957 became associated with research and development on polymeric organic materials and their application to all types of military equipment. As part of this work he was attached to U.S. Army Natick Laboratories, Natick, Massachusetts, during 1964-5.

At present Mr. Dunn is Head, Polymers Group, in the Organic Chemistry Division of DSL. His particular interests include studies on organotin compounds, on the stress cracking of polymers, and on the use of new rubbers, plastics and adhesives in adverse and often unusual environments.

hose for fuel lines; containers for ammunition; canteens for water; mechanical goods; tyres, treads and cushions for vehicles; stocks and butt plates for rifles; coatings for clothing and tarpaulins; surgical implants; film for wrapping material; composite plastics for personnel armour and rocket launch tubes; and fibres for flame-resistant clothing. Improvements are being sought continually to obtain better balance of weight-saving, cost-saving, and maximum serviceability. Depending on the particular end-item, polymeric materials may be required to exhibit such properties as oil resistance, water resistance, abrasion resistance, low-temperature flexibility, high-temperature resistance, dimensional stability, shock absorption, air retention, flame resistance, storage stability, and adequate dielectric strength.

In order to utilize polymers in military and industrial equipment to their best advantage, adequate performance in adverse environments is essential.

Performance at Elevated Temperatures

Linear and ladder polymers of either thermoplastic or thermosetting type can, when suitably formulated, form plastics materials of great versatility. One of the most important features of plastics is their heat (or thermal) resistance, and plastics of similar chemical composition but of different structure can show marked differences in their resistance to elevated temperatures. For instance, isotactic polystyrene has a melting point of 240°C whereas poly(para-xylylene), which has the same chemical composition but a different structure, has a melting point in excess of 400°C. Over the past decade a number of 'engineering-type' plastics have been introduced and these materials have been characterized by their improved heat resistance, especially in the range 300-600°C[1,2,3].

Three new types of polymers of particular interest are the aromatic polyimides, the polybenzimidazoles and the polyquinoxalines (Figure 1). The latter two types were mainly developed under military-funded projects.

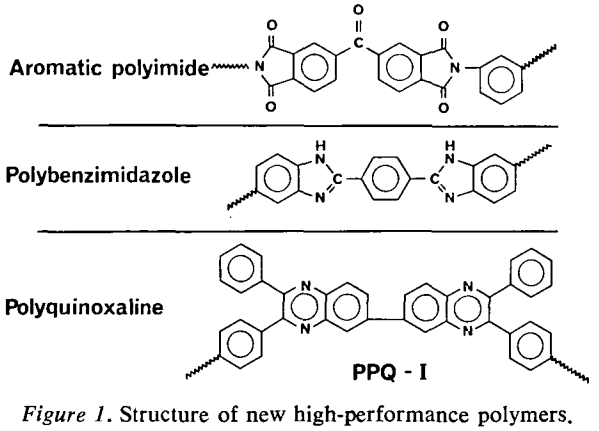


Figure 1. Structure of new high-performance polymers.

The polyimides and polyquinoxalines are essentially used as laminating resins, for applications where high temperature resistance is required. Recently a new class of crosslinked polyphenylamidequinoxalines has been developed; these materials are readily processable and have excellent temperature resistance. A drawback of the linear structure is that they become thermoplastic above the glass transition temperature (between 330-370°C). For high temperature composite applications this is undesirable, and to overcome this problem a new modified amide-quinoxaline polymer has been synthesized which has crosslinking sites built into the main chain. These are reactive at higher temperatures during moulding, and result in the formation of a crosslinked thermosetting resin.

Polybenzimidazole (PBI) has been used in the development of non-flammable fibrous materials, and fabrics woven from PBI fibres are now gaining wide acceptance in many military applications. Although resistance of a polymer to elevated temperatures is a desirable requirement in order to promote non-flammability, this characteristic alone is not sufficient. Once a polymer has reached an elevated temperature, the mechanism of pyrolysis and the nature of the resultant byproducts will determine the degree of combustibility of the material. Although PBI polymers and some aromatic polyamides show similar resistance to elevated temperatures, the improved resistance to burning of PBI fabrics ensures their use in many demanding applications.

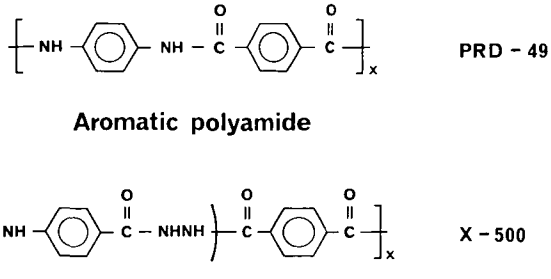


Figure 2. Structure of new aromatic polyamides.

The recent discovery of very high-modulus fibres based on aromatic polyamides[4] is claimed to be "a quantum jump in the technology of organic fibres". Chemically the fibres are almost wholly aromatic and two typical polymers are shown in Figure 2. Although a large number of aromatic polyamides are possible, a high proportion of para-substituted groups leads to a high melting point, less soluble polymer and to fibres of high modulus. These polymers are generally intractable and the final choice of material is made to provide the optimum balance of polymer processability and fibre strength and modulus. Both PRD-49 and Fibre X-500 (Figure 2) are currently being evaluated in a wide

range of military, industrial and consumer applications. The aim of these evaluations is to capitalize on the high strength (3.4 GN m^{-2}, 500,000 lbf in^{-2}), low elongation at break (2.1%), low density (1.45 g cm^{-3}), excellent resistance to water (92% strength retention after immersion at 50°C for 180 days), and high heat resistance (less than 0.1% shrinkage after exposure for 5 min. at 400°C) of the fibre (data for PRD-49). These fibres have considerable potential for use in tyres, armour, laminates, fabrics, cables and in ropes, twine and cordage.

In some instances the deterioration of organic materials at elevated temperatures is used to advantage. The formation of high strength carbon fibres from the pyrolysis of polyacrylonitrile is a typical example. Kilpin[5] has discussed the chemistry of the reactions involved, and James and Le Maistre[6] have described the use of carbon fibres in composite materials, many of which are designed to function in very adverse environments.

Speciality Rubbers

A wide range of synthetic rubbers is available for use in critical applications, including styrene-butadienes, butadiene-acrylonitriles, polychloroprenes, polyacrylics, chlorosulphonated polyethylenes, ethylene-propylene copolymers and terpolymers, silicones, fluoroelastomers, polyepichlorohydrins, polysulphides, butyls and others. Over the past decade most work has been directed at improving the performance of existing materials, by polymer modification or by changes in formulations. This type of work is expected to continue.

Although many classes of rubbers are available, limitations in performance at low temperatures (below —100°C), at high temperatures (above 300°C), and in certain aggressive environments still create serious problems for the designers of sophisticated equipment. The introduction of the nitrosorubbers[7] (Figure 3) enabled rubber vulcanizates with excellent chemical resistance and with non-flammable characteristics (even in pure oxygen atmospheres) to be produced. These are used in high-performance applications such as cable insulation, seals, 'O' rings and expulsion bladders.

Another new class of synthetic elastomer, known as polyphosphazene rubber, is shown in Figure 3. The successful synthesis of high molecular weight, stable polyphosphazene polymers with a phosphorus-nitrogen backbone is one of the most important developments in the field of inorganic polymers in recent years[8]. The potential areas of application of this class of polymers include low-temperature rubbers for POL handling equipment, non-flammable coatings for marine and aircraft uses, and seals and gaskets with good high- and low-temperature capability and chemical resistance. The development of non-combustible and non-corrosive lubricants and hydraulic fluids from low molecular weight polyphosphazenes is another promising area.

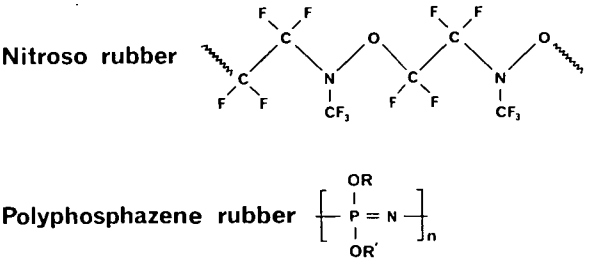


Figure 3. Structure of recently-developed speciality rubbers.

Polyphosphazene rubbers and fluids are made from low-cost, readily available materials (Figure 4). A major breakthrough in their development was the discovery of the method of purification of the low molecular weight polymer, $(PNCl_2)_n$. When this polymer is reacted with fluoroalkoxy, amine or aryloxy groups, substitution of the chlorine occurs to form the appropriate poly(fluoroalkoxy, amine or aryloxy) phosphazene. The latter class of compounds is inexpensive and they are being developed as flame-retardant materials for use in marine applications. Further work on the characterization and synthesis of polyphosphazenes is being undertaken, together with a study on the commercial potential of the materials.

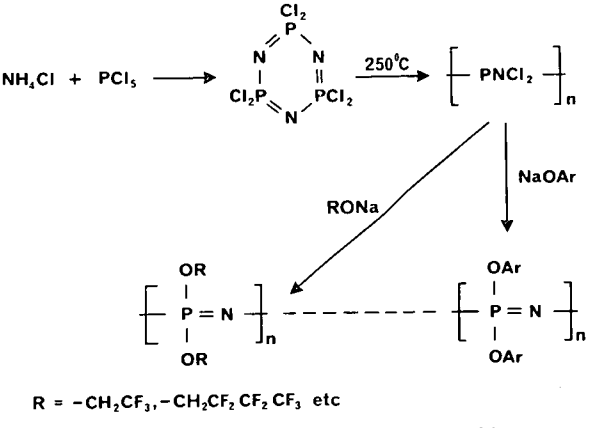


Figure 4. Synthesis of polyphosphazene rubbers.

Typical properties of four classes of rubbers are set out in Table 1. Both the silicone and polychloroprene types are widely used in a variety of industrial applications, the nitroso rubbers have selected special uses, and the polyphosphazenes are being evaluated. Their attraction is the combination of special properties such as chemical resistance and low-temperature performance, coupled with their potentially low cost and availability. Their versatility in being available in forms ranging from low viscosity fluids to tough, highly elastic rubbers is an added attraction.

Table 1

Properties of Speciality Rubbers

	Phosphazenes	*Nitroso*	*Silicones*	*Polychloroprenes*
Volume swell, %*	7	2	200	80
Low temperature limit, °C†	—70	—40	—40 to —70	—20
High temperature limit, °C†	200	150	250	130
Tensile strength, MN m^{-2}	10	8	4-8	20
Flammability	No	No	Yes	Yes
Cost, $/kg	15-20‡	High	3-5	Less than 1

* In a typical isooctane-toluene reference swelling fluid
† For continued service under operational conditions
‡ Estimated

Stress Cracking of Polymers

Where premature failure of a polymer occurs in the presence of stress and an adverse environment together, then failure is known as environmental stress cracking. Rosen[9] has described typical fracture processes in polymeric materials, including stress cracking.

At Defence Standards Laboratories we have studied the stress cracking of polyamides (nylons) by a range of metal salts, including halides, thiocyanates[10] and nitrates[11]. Although many organic polymeric materials are affected by organic solvents, the rupture of nylons by inorganic chemicals is unusual. Nylons are also often used in many industrial applications where they could be in contact with metal salts which could cause serious failures.

Many metal halides and halide-like salts were found to be active stress-cracking agents, while metal acetates and sulphates were inactive. Salts of zinc, calcium and lithium were found to be active stress-cracking reagents. The rupture of nylons by these agents was found to be dependent on temperature, moisture content of the nylon, concentration of the cracking agent and level of stress, and as these increased so did the rate of cracking. Metal halides did not appear to cause chain scission in the nylon and stress cracking was not due to hydrolysis or to metal-ion catalysed hydrolysis.

Two types of changes were observed, depending on the metal halide involved, and on this basis the metal halides were classified as Type I or Type II. Type I metal halides, such as zinc, cobalt, copper and manganese chlorides, form complexes in which the metal atom is coordinately bonded to the carbonyl oxygen atom of the amide group of the nylon. These agents cause stress cracking by interference with the hydrogen bonding in the nylon. Type II metal halides, such as lithium, calcium and magnesium chlorides and lithium bromide, in solution form proton-donating, solvated species which act as direct solvents for nylon 6 in a manner similar to phenols and formic acid. Type II agents appear to cause simple solvent cracking.

All nylons absorb water to some degree, and the equilibrium water content was found to have a significant effect on the rate of cracking of nylons by metal salts. Where the water content is greater than 1-2% by weight, a serious stress-cracking hazard in nylon can exist. Moulded specimens of different types of nylons were exposed in the jungle at the Joint Tropical Research Unit, Innisfail, and the water uptake over a period of several months was determined. The results, shown in Figure 5, indicate that only nylon 11 (polyundecanoamide) has an equilibrium moisture content, under field conditions, of less than 2%. Practical experience has confirmed that this type of nylon, together with nylon 12, is generally resistant to stress rupture by metal salts.

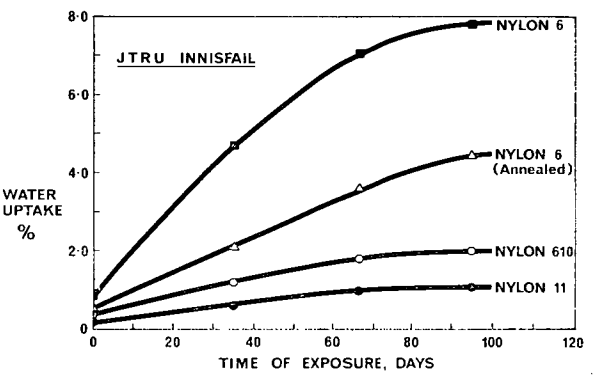


Figure 5. Relationship between water uptake of nylons and time of exposure, for specimens exposed in the 'jungle' at JTRU, Innisfail, North Queensland.

Flammability of Polymers

The increased utilization of polymers in the building and transportation industries has stimulated research and development aimed at reducing the flammability and smoke-producing properties of a wide range of organic materials. As many of these materials are used to give protection against corrosion, or to provide a decorative finish to components based on steel, stone or concrete, it is essential that materials with a high degree of flame resistance be used. A new scientific journal primarily devoted to this subject has recently appeared[12].

Although some polymers such as poly(vinylidene chloride) and polytetrafluoroethylene have good flame resistance, other polymers need to be modified by formulating, in order to impart an acceptable degree of

esistance. Fillers containing bromine, chlorine, antiony and phosphorus are widely used in selected ombinations aimed at producing synergistic effects. Recently a seminar[13] entitled *Fire Performance of Plastics* was held in Melbourne to discuss many of the urrent problems.

New techniques have recently been developed to assess he flammability and smoke-producing properties of rganic materials. The General Electric Flammability ndex Tester[14] is a device which determines the relative lammability of materials by a very sensitive and reproucible technique. Unlike most traditional measures of lammability, the new technique depends on a variable vhich can be measured precisely — the minimum olume concentration of oxygen required to support he combustion of a material sample. This minimum alue is described as the Limiting Oxygen Index and an be determined to an accuracy of better than one ercent of the index. For 'self-extinguishing' materials he Limiting Oxygen Index is expected to be equal to r greater than 27%. The oxygen index ratings of ome typical polymers are given in Table 2.

Table 2

Oxygen Index Ratings(%) of Polymers		
Poly(methyl methacrylate)	17.3	
Polystyrene	18.3	
ABS/polycarbonate alloy	20.2	(air equivalent)
Nylon 66	28.7	
Poly(vinylidene chloride)	60.0	
Polytetrafluoroethylene	95.0	

n a fire situation the amount of smoke generated due o the combustion of polymeric materials can be conideration and efforts are now being made to synthesize olymers which will produce minimum smoke on urning. Recently a new technique[15] has been introduced to enable the smoke-producing characteristics of olymers to be measured under controlled conditions f combustion. Measurements are made in terms of the oss in light transmission through a collected volume of moke produced under controlled, standardized conditions. The technique may be used for evaluating smoke roduced by wood, paper, fabrics and other organic naterial. A typical result (Figure 6) shows the effect f chemical composition on smoke development resulting from the combustion of a standard polyurethane oam and of a polyisocyanurate foam.

Polymers with a high degree of resistance to flame and with associated low levels of production of smoke on urning will be developed by chemical modification of he basic high molecular weight polymeric structure, or example, the development of polybenzimidazoles (Figure 1). These inherently fire-resistant polymers

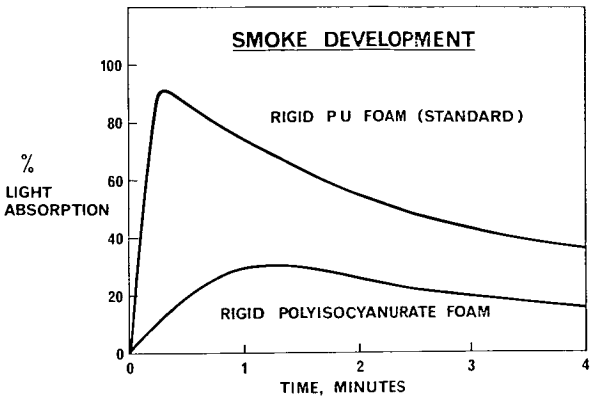


Figure 6. Effect of chemical composition on smoke development resulting from the combustion of rigid polyurethane foams.

should result in a reduced need for special additives to impart flame resistance to polymers which are known to be flammable. Associated problems concerned with toxic or corrosive combustion should also be reduced.

Armour, Weathering and Radiation

The greater utilization of organic materials in lightweight armour in the future is an attractive possibility. At present two classes of armour make use of polymeric materials; these are the hard-faced composite (HFC) armour systems and the fabric-based armour systems.

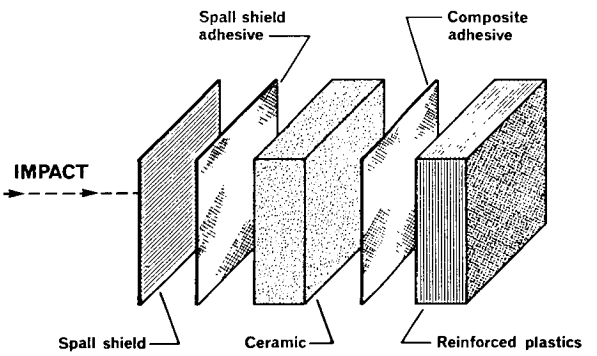


Figure 7. Typical hard-faced ceramic (HFC) armour system.

As shown in Figure 7, a typical ceramic composite armour system (HFC) consists of five major components, and of these four (spall shield, spall shield adhesive, composite adhesive and reinforced plastics back-up plate) are based on polymeric materials.

Essential to the overall performance of the armour is the design and construction of the back-up plate. This is usually made of polyester resin reinforced with specially treated woven glass-fibre fabric. Improvements in resin and reinforcing fibre may lead to slight weight reduction, but of greater importance is the possi-

bility of improved ballistic performance coupled with a minimum increase in weight. The symposium report by Wittman and others[16] describes recent developments in armour for men and vehicles.

The influence of the outdoor environment (weathering) and of ionizing radiation on polymers can cause marked changes in the chemical, physical and mechanical properties of these materials. The reports by Pinkerton[17] and Sangster[18] describe recent developments of interest in these two specific areas.

Conclusions

As polymeric organic materials of all types become more widely used in military, industrial and consumer applications, they will be required to perform satisfactorily in a wide range of adverse environments. Plastics, rubbers, adhesives, textiles, coated fabrics, sealants, and paints will be developed with improved resistance to low and high temperatures, to organic and inorganic chemicals, to biological attack of all types, to weathering, and to severe conditions of mechanical abuse.

These improvements in overall performance will be achieved by variations in the morphology of the basic polymer system, by improvements in processing techniques to enable components to be produced with optimum chemical, physical and mechanical properties, by chemical modification of the polymer, by the use of improved stabilizer systems, and by the development of better fillers and reinforcing materials.

References

1. H. Lee, D. Stoffey and K. Neville: "New Linear Polymers". McGraw-Hill, New York, 1967.
2. J. Idris Jones, *Chem. Brit.*, **6**, 251 (1970).
3. J. H. Hodgkin, *Proc. Roy. Aust. Chem. Inst.*, **38** (1), 21 (1971).
4. Anon., *Chem. Eng. News*, **50** (16), 33 (1972).
5. D. Kilpin, *Proc. Roy. Aust. Chem. Inst.*, **39** (5), 141 (1972).
6. B. H. James and C. W. LeMaistre, *Proc. Roy. Aust. Chem. Inst.*, **39** (6), 187 (1972).
7. C. B. Griffis and M. C. Henry, *Rubber Chem. Technol.*, **39** (3), 481 (1966).
8. G. Allen and R. M. Mortier, *Polymer*, **13**, 253 (1972).
9. B. Rosen (Ed.): "Fracture Processes in Polymeric Solids — Phenomena and Theory". Interscience Publishers, Inc., London, 1964.
10. P. Dunn and G. F. Sanson, *J. Appl. Polym. Sci.*, **13**, 1641 (1969).
11. P. Dunn and G. F. Sanson, *J. Appl. Polym. Sci.*, **14**, 1799 (1970).
12. *Journal of Fire and Flammability*. Technomic Publishing Company, Stamford, U.S.A. Vol. 1, 1970.
13. *The Fire Performance of Plastics*. Report of a Seminar sponsored by the Plastics Institute of Australia Inc. and held in Melbourne, 13 November, 1972.
14. "Standard Method of Test for Flammability of Plastics Using the Oxygen Index Method". ASTM D-2863. American Society of Testing and Materials, Philadelphia, U.S.A.
15. "Measuring the Density of Smoke from Burning or Decomposition of Plastics". ASTM D-2843. American Society of Testing and Materials, Philadelphia, U.S.A.
16. R. E. Wittman and others: *Symposium on Lightweight Armour*. Advances in Structural Composites, Papers A1, A2, A3 and A4. 12th National Symposium, Society of Aerospace Material and Process Engineers, Anaheim, California, 1967.
17. D. M. Pinkerton, *Proc. Roy. Aust. Chem. Inst.*, **39** (1), 33 (1972).
18. D. F. Sangster, *Proc. Roy. Aust. Chem. Inst.*, **39** (4), 110 (1972).

CSIRO Appointments

Recent appointments to CSIRO Divisions include the following:

DR. W. W. BARKER, *Associate,* formerly of Victoria, has transferred to the Western Australian laboratories of the Division of Mineralogy, at Wembley.

MR. S. Y. IP, *Associate,* has transferred from Victoria and is now employed as a Scientific Services Officer at CSIRO Head Office, A.C.T.

MR. D. E. PETERS, *Associate,* having joined the Division of Protein Chemistry as a Research Scientist, has transferred from N.S.W. to Victoria.

DR. L. J. WARREN, *Associate,* a former Queensland member, has taken up a position as a research scientist with the Division of Mineral Chemistry, Port Melbourne.

DR. I. A. WEEKS, *Associate,* has joined the Division of Applied Chemistry, Fishermen's Bend, Victoria, as a postdoctoral Fellow working on a National Research Council of Canada Grant. He was formerly a Tasmanian member.

APPENDIX 28 SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPDM) RUBBERS

28a Test Data on Vulcanizates - Hardness 28.2

28b Specimens of EPDM and Nitrile-PVC Vulcanizates 28.3

The vulcanizates were prepared by the author in September, 1964 at US Army Natick Laboratories Natick, Massachusetts, USA. They were returned to Materials Research Laboratories, Department of Defence, Melbourne in May, 1965 and since that date have been stored in the dark under normal laboratory conditions. The vulcanizates were tested in 1970 and 1978 and mounted in May, 1978. Test data for the vulcanizates are summarized at Appendix 19c. The protective film used as part of page 28.3 is poly(ethylene terephthalate) *(Melinex*, ICI Australia Ltd) and the vulcanizates were bonded into the cardboard holding frame using methyl cyanoacrylate adhesive *(Eastman 910)*.

Because of the historic nature of these non-black, silica-reinforced EPDM rubbers, they have been included in this document. The specimens are the last remnants of the original test sheets and are believed to be some of the oldest high quality, non-black EPDM vulcanizates in existence. They will be of future interest because they should give an indication of the actual long-term performance of such vulcanizates.

Technical details of the vulcanizates appear in Section 9, page 46 and at Appendix 19 (a, b and c).

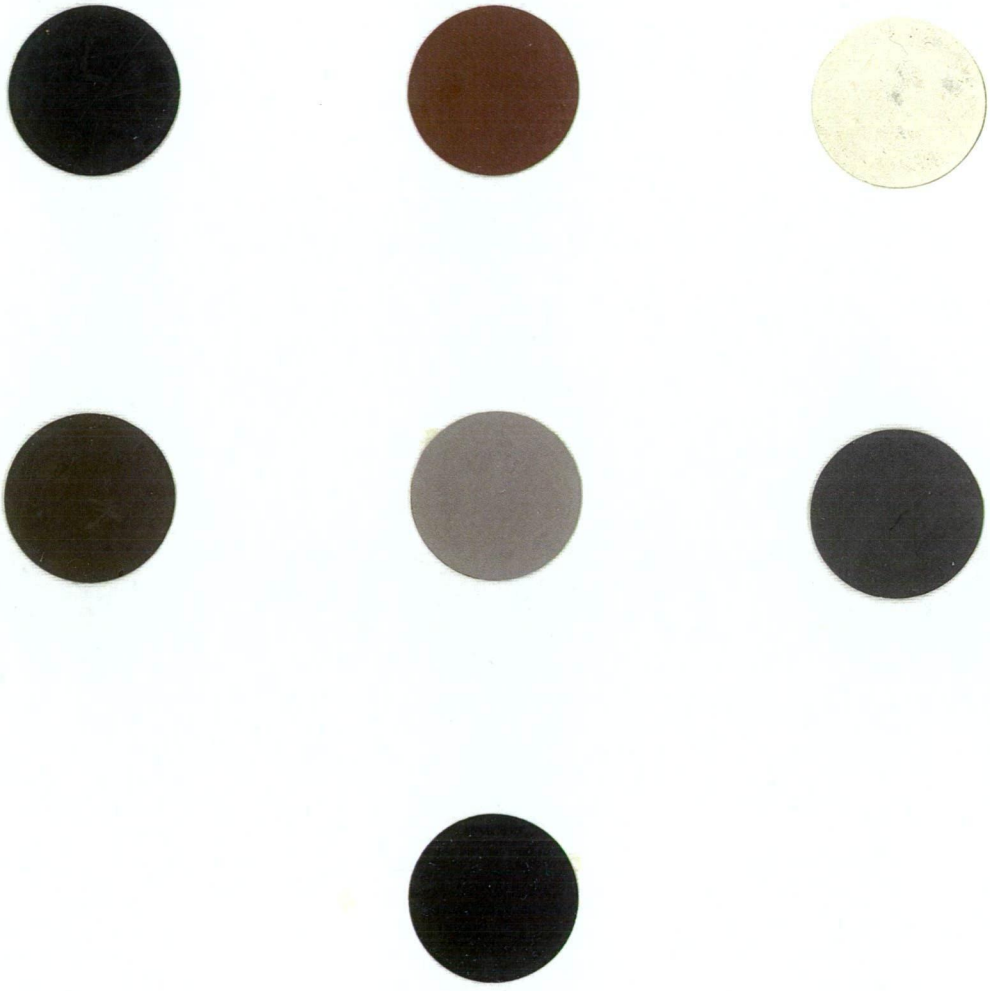
APPENDIX 28a TEST DATA ON VULCANIZATES - HARDNESS

Hardness	Shore Durometer A*			Rex Durometer A**		
Vulcanizate	Sept., 1964 As Moulded	Sept., 1970 Aged, 6 yr	Jan., 1978 Aged, 13.3 yr	Sept., 1978 Aged, 14 yr	Future	Future
EPDM						
Black (92)	59	66	67	66		
Red (189)	57	62	65	65		
White (190)	56	63	65	66		
Olive drab (191)	59	62	65	66		
Light grey (192)	57	62	63	65		
Dark grey (193)	58	62	63	65		
NITRILE-PVC						
Black (194)	71	84	89	89		

* Instant reading (at 22°C) of durometer on ends of three dumb-bells layered up.

** Rex Durometer, Model 1700, Rex Gauge Company, Glenview, Illinois. Hardness measurements were made on single-layer specimens mounted in the cardboard frame as shown on page 28.3. An aluminium backing sheet, 1.5 mm thick, was placed behind the mounted specimens to provide support. A calibration curve for Type A Durometers is given in ASTM D 2240 (239).

Appendix 28b - Specimens of EPDM and Nitrile-PVC vulcanizates for long-term ageing studies: moulded September, 1964; mounted May, 1978.



CODE

Black (92)	Red (189)	White (190)
Olive (191)	Light grey (192)	Dark grey (193)
	Black (Nitrile-PVC, 194)	